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OUTLINES

OF

THEORETICAL CHEMISTRY

OUTLINES
OF
THEORETICAL CHEMISTRY

BY

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WITH A PREFACE BY THE AUTHOR

SECOND EDITION

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AUTHOR'S PREFACE TO ENGLISH TRANSLATION

As Messrs. Bedson and Williams some years ago made a careful and accurate translation into English of my 'Modern Theories of Chemistry,' I very gladly accepted their friendly proposal to undertake the translation of this smaller book.

It may appear somewhat doubtful whether the long-felt want of a small text-book on theoretical chemistry has not been satisfied by the books recently published by Polis, Remsen, and Ostwald. These books are themselves so different from one another and from mine in method and intention and in their conclusions, that they all may be able to exist side by side. This conclusion is satisfactorily confirmed by the ready reception which the German edition of my book has received.

In writing this work I have not considered the requirements of students alone, but have been desirous of offering something to those friends of scientific investigation who have neither the intention nor the time to concern themselves with the details of chemical investigation, but wish to become acquainted with the general conclusions arrived at.

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With this object in view I have abstained from too large a use of the numerical results of observations and measurements, and have avoided giving detailed descriptions of experimental methods.

This book has, therefore, in the main, been written from memory, and numerical examples have been taken from the existing literature only where it appeared absolutely necessary for the clearer understanding of the subject. The general—I may say the philosophical—review of the subject has been my chief aim, to which the details should be subordinated. I may, perhaps, be permitted to express the hope that this mode of treatment will especially meet with approval in England, where so wide a circle of readers interest themselves in the general results and conclusions of scientific investigations.

LOTHAR MEYER.

TÜBINGEN: *December* 30, 1891.

TRANSLATORS' PREFACE

The reception which our translation of Lothar Meyer's 'Modern Theories' met with has encouraged us to present to the public an English version of the author's smaller and less technical work on Chemical Philosophy.

The revised sheets have been submitted to the author, and we have gladly availed ourselves of the valuable suggestions he has made. As the nature of the book is set forth in the author's preface specially written for this translation, there remains only to add that we trust this book may not only be found valuable to the student of chemistry, but also to those who are interested in science generally.

THE TRANSLATORS.

January, 1892.

PREFACE

TO

THE SECOND EDITION

In preparing a second edition of the translation of Meyer's 'Outlines of Theoretical Chemistry,' we have in the revision availed ourselves of the second edition of the German, published in 1893, a few years before the death of Lothar Meyer. Whilst the original form has been still retained, we have, by occasional footnotes and appendices, sought to bring the book up to date.

Our thanks are due to Dr. J. A. Smythe, who has kindly assisted in reading the proof pages for this edition, and also to Sir William Crookes, and to the Council of the Royal Society for permission to use the diagram illustrating the position of argon, helium, and krypton in the scheme of elements.

July 1899.

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OUTLINES
OF
THEORETICAL CHEMISTRY

UNIV. OF CALIFORNIA

§ 1. **Definition and Province.**—Chemistry is a most important branch of natural science. As the mind is incapable of embracing knowledge in its entirety, it is necessary to divide science into several branches. The sciences may be classified either according to the methods of investigation employed or according to the objects investigated. In the first system we distinguish between descriptive science, sometimes inaptly termed natural history, and natural philosophy, which should in reality be styled natural history.

The investigation and description of the various objects as they occur in nature form the problem with which the descriptive sciences deal, whilst it is the aim of natural philosophy to investigate their genesis and transformations, and to endeavour to discover the cause of these changes. Chemistry[1] belongs to both branches of science.

If we examine any natural object, such as a rock, an animal, or a plant, we find, as a rule, that it is composed of many dissimilar parts. The rock is composed of different minerals, the animals and plants are of different organs; these, again, are built up from more elementary forms, such as cells, &c. But this subdivision cannot be carried on indefinitely, for we finally arrive at forms of matter which cannot be split up by mechanical means into dissimilar particles. Chemistry is the science which investigates and describes these ultimate constituents, of which all natural objects are composed. Chemistry is, therefore, a fundamental portion of all descriptive science.

---

[1] The origin of the word 'chemistry' is not known with certainty.

But, on the other hand, chemistry is also one of the explanatory sciences. Almost all the natural phenomena with which we are acquainted are of a complex nature; the eruption of a volcano, an earthquake, a thunderstorm, a fire, the life and growth of animals and plants, and numerous other occurrences, are the combined effect of several distinct phenomena, such as light, heat, sound, electricity, evaporation, and other changes of condition. Natural philosophy treats of these elementary changes into which natural phenomena resolve themselves. Natural philosophy embraces physics and chemistry. It is the aim of physics to investigate and explain those elementary changes which affect the properties of bodies without altering their material composition. Chemistry deals with the changes which affect the material nature of the substance. Chemistry, then, is the science which treats of matter and its changes.

§ 2. **Characteristics of Chemical Change.**—Numerous material changes in natural objects are continually taking place, such as the formation of organic compounds in plants, the various changes which animal and vegetable bodies undergo either in nature or such as are produced by the agency of man; for example, fermentation, putrefaction, combustion, the extraction of metals from their ores, the preparation of food, drugs, dyes, and innumerable other materials. These changes in the composition of bodies have been occurring from time immemorial before the eyes of men, generally, indeed, at man's desire; but in spite of this, for thousands of years they have been involved in obscurity, and even at the present time they remain incomprehensible to the majority, even of educated people. Although chemical changes are continually taking place everywhere, the cause of these changes is difficult to recognise. This peculiarity of chemical phenomena is an inherent result of their nature. By exposing one or more substances to certain conditions, an entire change in their nature is effected. This may be brought about by exposing the substance to the action of heat, light, or percussion; indeed, in some cases a chemical change takes place when the substance does not appear to have been subjected to any kind of external influence. Sulphur burns, and leaves in its place a pungent-smelling gas. Coal is heated, and produces coal gas, ores are heated with charcoal and yield metals. Iron rusts in the air, molten lead changes into a dull powder called litharge, which is reduced to lead when heated with charcoal. These changes, and thousands of similar transformations, were regarded and treated as mysteries.

Compare these changes with such phenomena as the movement of a falling body, the reflection or refraction of a ray of light, the heating and cooling of a body, the action of one magnet on another, &c., and we see that it is not very difficult to study the entire course of such physical phenomena; whereas in the case of chemical changes the beginning of a reaction is, as a rule, immediately followed by its conclusion, so that it is impossible to perceive the intermediate stages. For this reason chemistry remained for thousands of years a mere collection of recipes and mystic formulæ, in spite of the labour which had been devoted to its advancement. This explains also how chemistry should have existed for centuries in a condition hardly worthy of the name of a science, side by side with a highly developed state of physics.

§ 3. **Method of Investigation.**—The high state of development to which science has attained at the present day has been gained by a logical application of the method of induction. The numerous isolated facts presented to our observation are so classified, that allied and analogous facts are arranged together for the purpose of comparison. The laws and rules resulting from this comparison are gradually expanded and generalised, or, if necessary, more sharply defined, and their application limited. The knowledge of such laws does not satisfy the human mind—it desires to learn the reason, the cause of the existence of these laws.

Now, this knowledge cannot be gained from observation alone, but by an effort of our intellect the connection between the phenomena under observation and the causes which produce and modify them are solved.

The knowledge of the causal connection of phenomena is consequently subjective, and it always remains an open question to what extent it is co-ordinated to the objective world. The investigation of this point is a second problem for science to solve. We proceed by assuming more or less arbitrarily a certain cause for each group of phenomena. Then, without reference to facts, we proceed to draw or 'deduce' all the conclusions that can be logically developed from the 'hypothesis.' We call this development the theory of the events in question. A comparison of the theoretical deductions with the observed facts is the sole means of judging the correctness of the theory and of the hypothesis on which it is based. So long as facts and theory agree, we are justified in regarding the theory as accurate, but not as absolutely and infallibly true.

If the theoretical conclusions and the facts do not agree, then the hypothesis is false, or the extension of the theory has been incorrectly carried out, and the errors must be sought out and corrected. Hypotheses and theories contradicted by observation must be rejected; doubtful theories may often be usefully retained so long as they facilitate the survey of a large number of observations. The best supported theory must never be regarded as absolutely true, a high degree of probability is the utmost that can be claimed for it.

As examples of a few of the hypotheses which have attained this highest degree of probability we may mention Newton's hypothesis that the heavenly bodies exert a mutual attraction on each other which is inversely proportional to the square of their distances; Huygen's hypothesis that light is an undulatory movement of the ether; and the hypothesis of Daniel Bernoulli and R. Clausius that in the gaseous state the particles are in rapid rectilinear motion.

If we ask how far a happily chosen hypothesis or a correct theory can carry us on the path of knowledge, we find we must be content if, by their aid, we can follow and discern the causal connection and the necessary results of phenomena until we arrive at certain values which remain unaltered in the various changes. These unchangeable values are termed 'constants.' They may be real values or only express proportions or ratios of such things as number, weight, length, space, or time. A 'constant' is not of necessity absolutely invariable, it is sufficient for our purposes if it does not undergo any appreciable change in the phenomena under investigation. Consequently the constants we arrive at, in a certain group of phenomena, need not of necessity form the limits of our knowlege, but may in turn form the subject of research, for the investigation of the conditions under which they vary may lead up to constants of a higher order. But in spite of all the progress we have made, the determination of the constants still remains the problem for investigation. We are content when we succeed in predicting the phenomena which result as a natural consequence from certain constants, and the varying relations which these constants bear to one another.

§ 4. **Development of Chemical Theories.**—The inductive method was first applied in chemistry at a comparatively late stage in its history. It was only at the end of the seventeenth, and more particularly during the eighteenth century that all the then known facts were systematically arranged and a logical classification of bodies into combustible and incombustible, burnt and unburnt, was made. The hypothesis which was employed to account for the difference between these two large classes of bodies proved ultimately incorrect. This hypothesis assumed the existence of a peculiar combustible principle, the so-called 'phlogiston,' in all combustible substances. Combustion consisted in the evolution of phlogiston. In recent times it has been shown that the phlogiston theory is not altogether devoid of truth, for what was formerly termed phlogiston is almost identical with our present notion of potential energy. It was during the two hundred years when the phlogiston theory prevailed that the application of inductive methods revealed the general truth that matter can neither be created nor destroyed. This discovery led to conclusions rendering the doctrine of phlogiston untenable, and resulting in its replacement by Lavoisier's theory of combustion. According to this theory the process of combustion is not due to an evolution of phlogiston, but to 'oxidation'—that is, to the combination of the combustible body with oxygen, one of the constituents of atmospheric air.

During the period of quantitative analysis, which begins with this theory, great stress was laid on the investigation of the proportions by weight in which different substances unite together, and thus a new field of research was opened up which rapidly acquired unexpected dimensions.

The most important result of this new development was to strengthen our knowledge of the fact that nothing is lost and nothing is gained when substances undergo chemical change. When substances unite together the weight of the compound is exactly equal to the sum of the weights of the constituents. The recognition of this principle and its application served to simplify many of the difficult questions concerning the composition of bodies produced in various ways. When red-hot iron is hammered it yields forge-scales, and on exposure to damp air it rusts. In either case it gains in weight; consequently it has combined with something, and not lost anything as was formerly supposed. It has combined with oxygen, and the increase in weight is equal to the weight of oxygen the metal has united with in its conversion into oxide (rust or forge scales). Consequently the oxide is the compound and the metal is a constituent; but in the last century the reverse was held to be the case. In this way 'quantitative chemistry' effected an accurate distinction between elementary bodies and their compounds, and imparted a degree of exactness to the methods of investigation, of which in previous centuries there had been no conception.

We are acquainted with about seventy bodies which have up to the present time resisted all attempts to decompose them. We therefore consider these substances as invariable in composition until the contrary is proved, and consequently regard them as the fundamental constants of chemistry. The aim of the science of chemistry is to investigate the laws which govern the combination of these elements, and to determine in what way the character and properties of the compounds are affected by the nature of the constituent elements.

§ 5. **Stœchiometric Laws.**—The further investigation of the quantitative composition of chemical compounds led to the foundation of the science of stœchiometry[1] by Jeremias Benjamin Richter. The most important facts of stœchiometry were discovered almost simultaneously by Proust. The fact pointed out by Proust, that definite chemical compounds always contain their constituents in fixed and invariable proportions, was strongly disputed by no less an authority than C. L. Berthollet.

---

[1] *τὰ στοιχεῖα*, the constituents. *τὸ μέτρον*, the measure.

Richter's views on the laws which govern the combination of acids with bases to form salts remained for a long time neglected and almost unnoticed. The credit of establishing the value of these laws (so far as they were correct) belongs to J. J. Berzelius, who obtained important aid from an hypothesis propounded by John Dalton.

The fundamental law of stœchiometry, discovered by Richter and confirmed and developed by Berzelius, states that all true chemical changes (*i.e.* changes of composition) take place between definite volumes or weights of the substances. This is equally true whether a substance decomposes into its constituents or is formed from its constituents, or when different compounds exchange one of their constituents.

When water is formed from its constituents 7·98 parts by weight of oxygen unite with one part by weight of hydrogen, never more nor less, and the two constituents are produced in exactly these proportions when water is decomposed.

All other substances, whether elements or compounds, behave in the same way: that is to say, they only enter into combination or undergo decomposition in definite and fixed proportions by weight.

It often happens that the bodies unite together in several distinct proportions, but these different proportions always bear a simple relation to one another.

This empirical law is known as the law of multiple proportions. For example, there is another compound of hydrogen and oxygen, hydrogen peroxide, which contains 15·96 parts by weight of oxygen to 1 part by weight of hydrogen—that is, twice as much oxygen as unites with 1 part by weight of hydrogen in water. By mixing these two oxides of hydrogen a liquid is obtained in which the quantity of oxygen lies between that contained in water and in hydrogen peroxide. The resulting liquid is not a chemical compound, but merely a mechanical mixture, for its properties are those of its constituents, and the act of admixture is not followed by those changes in the material nature of the substances which are characteristic of chemical combination.

Nitrogen forms a larger number of oxides, in which one part by weight of nitrogen is combined respectively with 0·5696, 1·1392, 1·7088, 2·2784, and 2·8480 parts by weight of oxygen.

The relation between these quantities is expressed by the whole numbers 1, 2, 3, 4, 5.

The numbers indicating the proportions in which substances unite together are called 'combining weights,' or stœchiometric quantities. It is remarkable that they apply not merely to two given elements but to all elements without exception. For example, one part by weight of copper is combined with 0·1263 part by weight of oxygen in cuprous oxide, and with 0·2526 part by weight of oxygen (*i.e.* exactly double) in cupric oxide. The quantities of sulphur combined with one part by weight of copper in the sulphides are also in the proportion of 1 to 2, cupric sulphide containing 0·5062 and cuprous sulphide 0·2531 part by weight of sulphur; 0·2531 part by weight of sulphur on combustion unites with 0·2526 part by weight of oxygen. This is exactly the quantity of oxygen which unites with one part by weight of copper to form cupric oxide.

The combining weights for copper and sulphur and for copper and oxygen are also valid for the compounds of sulphur and oxygen. This rule is true of all elements. It may be generally expressed in the following words:

If we know the proportions by weight in which a series of elements unite with a certain given element, then these elements either unite with each other in the quantities represented by these proportions or in some simple multiple of them. If A, B, C, D represent the proportions by weight in which the different elements unite with a definite quantity of another element, then any compound of these elements can be represented by the formula

$$n \,.\, \mathrm{A} + n_1 \,.\, \mathrm{B} + n_2 \,.\, \mathrm{C} + n_3 \,.\, \mathrm{D} + \ldots$$

when n, n_1, n_2, n_3 represent whole (generally small) numbers.

The values A, B, C, &c. are the fundamental constants of stœchiometry.

§ 6. **Atomic Hypothesis.**—The stœchiometric laws are purely empirical, and were discovered by induction. They have been confirmed by thousands of experiments, and their validity is independent of any hypothesis. But man suspects a cause for every law, and is disinclined to acknowledge the existence of a law unless it can account for the cause of it.

Consequently the stœchiometric laws, which are now regarded as the most important ever discovered in natural science, were at first treated with neglect, until John Dalton investigated those laws and discovered a simple explanation of them.

Dalton investigated two gaseous compounds of carbon and hydrogen, and found that the so-called heavy carburetted hydrogen now called ethylene contained exactly half as much hydrogen combined with one part by weight of carbon as is the case in light carburetted hydrogen or marsh-gas. To explain this and similar observations concerning the oxides of nitrogen Dalton made use of an old and much-disputed hypothesis. He assumed that all elements consist of very minute indivisible particles, having a definite weight, termed atoms,[1] and that chemical compounds are produced by the union of these atoms.

This hypothesis was by no means new. More than two thousand years ago the Greek philosophers energetically debated the continuity of matter—whether matter completely fills the space it occupies, or whether it is composed of very minute individual particles separated from each other by spaces. These particles were termed atoms on account of their indivisibility.

Democritus and many others based their system of natural philosophy on these hypothetical atoms, and attempted to explain the transformations of the universe as the result of their properties and rapid movements. Aristotle and his followers could not tolerate the idea of the existence of an empty space between the atoms, but maintained that the whole space is completely filled with matter. This difference of opinion survived till recent times, but at the present day the truth of the atomic theory is no longer a matter of dispute. Dalton does not appear to have troubled himself about this discussion. He made use of the atomic theory because it enabled him to explain without difficulty the fact that the elements combine only in definite proportions by weight, and that if certain elements unite together in several different proportions these proportions bear a simple relation to one another. We assume that all the atoms of one and the same element have the same weight, but that this weight varies for different elements in the proportion of their stœchiometric quantities. Let A be the weight of the atom of a certain element, and B that of another; then it is obvious that a compound of one atom of the first with one atom of the second, *e.g.* A + B, must contain half as much of the second as another compound A + 2B.

---

[1] ἡ ἄτομος, the indivisible.

As all particles of such a compound have the same composition, then any number of particles or any given quantity of this substance will contain the constituents in the same proportion as the individual particles, viz. in the proportion of the atomic weights or in a simple multiple of them.

The atomic theory offers an exceedingly lucid explanation of the purely empirical law of combining proportions.

It is clear we can only deduce from the stœchiometric values the relative, not the absolute, weight of the atoms, as we only know the relative number of atoms contained in a compound. Black oxide of copper contains one part by weight of oxygen to 3·959 parts of copper. If we can by any means prove that this oxide contains an equal number of copper and of oxygen atoms, then it must follow that the weights of the atoms of these two elements are in the same proportion to each other that the constituents are in the oxide —namely, as 1 : 3·959. The copper atom is 3·959 times heavier than the atom of oxygen. This proportion by weight always remains the same, and is independent of the number of atoms of the elements entering into combination.

§ 7. **Symbols.**—Dalton imagined the atoms to be small spheres, and represented the atoms of different elements by various symbols enclosed in a ring or circle, thus :

1 Atom . .	Oxygen	Hydrogen	Nitrogen	Carbon	Sulphur	Phosphorus
	○	⊙	⦶	●	⊕	☮

Atoms of the metallic elements were represented by circles containing the initial letters of their names. Berzelius omitted the circle as inconvenient, and used the initial of the Latin name to represent the atom of any element. This system of notation is now universally adopted. Both Dalton and Berzelius placed two or more symbols side by side to indicate that the atoms had entered into combination.

The number of atoms is indicated by prefixing a numeral or by the use of indices. The device of Berzelius for representing a double atom by drawing a bar through the symbol is no longer used. Two atoms of hydrogen may be represented by the following symbols, 2H, H_2, H^2, HH. The second of these symbols is that most frequently employed.

§ 8. **Unit of Atomic Weights.**—We have already seen (§ 6) that the weight of the atoms cannot be deduced directly from the combining proportions, and that it is only possible to decide how many times heavier or lighter one atom is than another. This, however, is all that is requisite for the development of chemical theory. It is not necessary to know the weight of individual atoms. The composition of any mixture of different substances can be equally well expressed in grams, ounces, or pounds, and in the same way the composition of any chemical compound can be expressed in terms of any unit of weight that may be selected. If we choose the weight of an atom of a given element as unity, we can by means of the stœchiometric values express the atomic weights of the others in terms of this standard, so that a number is obtained for each element, which shows how many times heavier it is than the unit.

Dalton's proposal to take the atom of hydrogen, the lightest of all the atoms, as unity is at the present time universally adopted. But for many years it was the custom to follow the example of Wollaston and Berzelius, who, for certain practical reasons, took the atom of oxygen as their standard.[1] It is obvious that there will be a great difference in the atomic weights according to the standard selected. If hydrogen is taken as unity, it is clear that the atomic weights will be proportionally larger than is the case when the heavier atom of oxygen is taken as the standard. Just as in measuring distances, the numbers are larger if we reckon by feet instead of metres or by kilometres instead of miles. Now some atomic weights are smaller than that of oxygen, so in order to avoid fractions Wollaston took as his standard the tenth part, and Berzelius chose the hundredth part of an atom of oxygen, so that an atom of oxygen = 10 or 100. This standard yielded atomic weights which were in some cases larger than 1000, and are now no longer used.

§ 9. **Determination of Atomic Weights from Stœchiometric Values.**—We have already seen (§ 6) that the relative values of the atomic weights can only be calculated from the composition of a chemical compound as determined by synthesis or analysis, when the number of atoms contained in the compound is known. But the number of atoms cannot be directly determined, and can only be deduced by the help of hypotheses varying in degree of probability. Water is composed of oxygen and hydrogen in the proportion by weight of 7·98 : 1. It does not follow that the atomic weights of these elements are in this ratio, but only that the weight of all the hydrogen atoms in a given quantity of water bears this proportion to the total weight of the oxygen atoms combined with them, so that

$$n.\mathrm{H} : m.\mathrm{O} = 1 : 7{\cdot}98$$

when n and m represent whole (unknown) numbers. The atomic theory only teaches us that a certain number of whole atoms of one substance has combined with a definite number of whole atoms of a second element, *e.g.* $n\,\mathrm{H}$ with $m\,\mathrm{O}$. The values of m and n are not known. It is one of the most important problems in theoretical chemistry to determine the number of atoms which are united together in different compounds.

The solution of this problem was attempted immediately after the proposal of the atomic theory, but the possibility of a satisfactory solution was repeatedly and seriously contested. This dispute continued for upwards of half a century, and now at last we are in a position to maintain that the number of atoms in different compounds may be determined, if not with absolute certainty, at any rate with the greatest degree of probability.

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[1] At the present time, oxygen = 16 is generally taken as the standard.—TRANS.

§ 10. **First Attempts to determine the Atomic Weights.**—At first sight it would appear to be the simplest plan to regard the proportion by weight in which two elements unite together as identical with their atomic weights. But this is not possible, because many elements unite together in different proportions. In black oxide of copper one part by weight of oxygen is united to 3·959 parts by weight of copper; but in the red oxide, twice as much copper, viz. 7·918, is contained. Is the atomic weight of copper 3·959 or 7·918 times greater than that of oxygen? There does not appear to be any reason why one number should be selected in preference to the other. If we choose the first, then we have the formulæ

$$\mathrm{Cu\,O} = 3{\cdot}959 + 1, \text{ for the black oxide}$$

and

$$\mathrm{Cu_2\,O} = 7{\cdot}918 + 1, \text{ for the red oxide.}$$

If we take the second value, then we have

$$\mathrm{Cu\,O_2} = 7{\cdot}918 + 2, \text{ for the black oxide}$$

and

$$\mathrm{Cu\,O} = 7{\cdot}918 + 1, \text{ for the red oxide.}$$

Berzelius selected the second value, but it has been replaced by the first, which is now universally regarded as correct.

Dalton advocated the greatest simplicity; he assumed the existence of only one atom of each constituent in many compounds, in which, according to our present views, several atoms of one of the constituents are contained, *e.g.*

	Proportion by Weight.	Formulæ	
		Dalton.	Berzelius.
Water . .	1 : 7·98	HO	H_2O
Ammonia . .	1 : 4·67	HN	H_3N
Ethylene . .	1 : 5·985	HC	H_4C_2

According to Dalton's views, the atomic weights of oxygen, nitrogen, and carbon are to the atomic weight of hydrogen in the ratio of

$$O : N : C : H = 7{\cdot}98 : 4{\cdot}67 : 5{\cdot}985 : 1;$$

but according to Berzelius they stand to each other in the proportion of

$$O : N : C : H = 15{\cdot}96 : 14{\cdot}01 : 11{\cdot}97 : 1.$$

The values which Dalton regarded as the atomic weights of oxygen and carbon are only half, and in the case of nitrogen only one-third, of the values accepted by Berzelius.

§ 11. **Chemical Equivalents.**—At the beginning of the present century Wollaston proposed that the chemical symbols should represent the equivalents as determined by experiment. In this way he hoped to avoid the want of uniformity resulting from the use of the hypothetical atomic weights. Those quantities of different substances which produce the same, or nearly the same, effect were regarded as equivalent. The expression was originally applied to those quantities of different acids which are required to neutralise a fixed quantity of a given base, and also to those quantities of different bases which are required to neutralise a certain weight of a given acid. The expression was afterwards used in a wider sense, and was applied to all kinds of substances, including the elements. It is obvious that no element can be strictly equivalent to another. It is only equivalent in certain respects—namely, in its capacity for uniting with a third substance, or displacing it in a compound.

We regard as equivalent weights of the elements those quantities which have in this respect the same value, and we compare them as we do the atomic weights with one part by weight of hydrogen as unity. The equivalent weights of the elements are, therefore, those quantities of the elements which can enter into the same combinations as one part by weight or one atom of hydrogen, or can unite with one part by weight or one atom of hydrogen. The first definition holds good for the metals and semi-metals; the second is true of the non-metals, because all the latter can combine with hydrogen; but only a few of the metals are able to form hydrides.

By means of this definition the equivalent weights can easily be determined by experiment. One part by weight of hydrogen unites with—

19·06	parts by weight of	fluorine	4·67	parts by weight of	nitrogen
35·37	„	chlorine	10·32	„	phosphorus
79·76	„	bromine	24·97	„	arsenic
126·54	„	iodine	39·87	„	antimony
7·98	parts by weight of	oxygen	2·99	parts by weight of	carbon
15·99	„	sulphur	7·08	„	silicon
39·48	„	selenium			
62·50	„	tellurium			

One part by weight of hydrogen is replaced in its compounds by the following quantities of different metals. Of the lighter metals—

7·01	parts by weight of	lithium	4·54	parts by weight of	beryllium
23·00	„	sodium	12·15	„	magnesium
39·03	„	potassium	19·95	„	calcium
85·2	„	rubidium	43·65	„	strontium
132·7	„	cæsium	68·45	„	barium
			9·01	„	aluminium

The following quantities of the heavier metals expel one part by weight of hydrogen from water or hydrochloric acid, and replace it directly or indirectly:

27·4	parts by weight of	manganese	55·85	parts by weight of	cadmium
27·94	„	iron	59·4	„	tin
29·5	„	cobalt	103·2	„	lead
29·3	„	nickel	107·66	„	silver
32·55	„	zinc	203·7	„	thallium
37·8	„	indium			

These quantities of the metals will consequently be able to unite with the non-metals in the proportions stated in the preceding table—*e.g.* 35·37 parts by weight of chlorine, 7·98 of oxygen, &c.

Totally different results are obtained in the case of many metals if we determine directly the quantity of metal which will unite with one equivalent weight of oxygen (7·98 parts) or of chlorine (35·37 parts).

When iron is heated in chlorine, the equivalent weight of chlorine (35·37 parts), instead of uniting with 27·94 parts by weight of iron, only combines with $\frac{2}{3}$ of the quantity—viz. 18·63 parts. By the oxidation of metallic iron, one equivalent or 7·98 parts by weight of oxygen may combine 18·63 or 20·95 parts by weight of iron, according to the temperature and other conditions. In this way three different values are obtained for the equivalent weight of iron. Many other elements behave in a similar way; but the equivalent weights found by different methods always bear a simple ratio to one another. In the case of iron the values are:

$$18{\cdot}63 : 20{\cdot}95 : 27{\cdot}94 = \frac{2}{3} : \frac{3}{4} : 1 = 8 : 9 : 12.$$

If one of these values, for example 27·94, is arbitrarily taken as the true equivalent weight of this metal, the composition of all its compounds can be expressed by means of this equivalent.

		parts by weight		parts by weight		equivalent
Ferrous chloride	contains	27·94	iron, and	35·37	chlorine, or	1:1
Ferric chloride	,,	18·63	,,	35·37	,,	2:3
Ferrous oxide	,,	27·94	,,	7·98	oxygen, or	1:1
Ferric oxide	,,	18·63	,,	7·98	,,	2:3
Magnetic oxide	,,	20·95	,,	7·98	,,	3:4

Although any one of the various equivalent weights will suffice, it was soon found to be very difficult to decide which of these different values should be regarded as the true equivalent weight, and be represented by the chemical symbol of the element. For a long time the quantities of the non-metals contained in the first table were regarded as the true equivalent weights; but the values in the second table have never come into actual use. On the other hand, the equivalent weights for the metals contained in the table were, with the exception of those of beryllium and aluminium, in use for a considerable period.

§ 12. **Electrolytic Equivalents.**—The electrolytic law of Michael Faraday has been used to insure the uniform determination of equivalent weights. Faraday found that when an electric current is passed through a so-called conductor of the second class, an electrolyte (*i.e.* a substance which can only conduct electricity when it is decomposed by the current), the quantity of the substance decomposed is proportional to the intensity of the current.

If one and the same current passes through two electrolytes, then the several constituents deposited are electrically and chemically equivalent to one another.

To determine the equivalent weights of the elements by means of this law, it is only necessary to decompose some of their compounds by a current which simultaneously decomposes a hydrogen compound, and determine experimentally what weight of the given element has been liberated in the same time as one part by weight of hydrogen. On the whole, this method yielded more uniform results than those obtained by chemical analysis; but still different values were obtained for certain metals, according to the nature and composition of the compound investigated.

For example:—

Copper . .	31·59	and	63·18
Mercury .	99·9	„	199·8
Iron . .	18·63	„	27·94

Another difficulty presents itself. The compounds of many elements do not conduct electricity and are not decomposed by it, and consequently the determination of the equivalents by electrolysis is not universally applicable.

§ 13. **Crystallographic Equivalence. Isomorphism.**—In 1819 Eilhard Mitscherlich discovered the important law of isomorphism, which has been used by Berzelius and other investigators for the determination of equivalence. Mitscherlich found that certain elements can replace others in their compounds without producing any essential alteration in the crystalline form of the substance.

These compounds and the elements which mutually replace each other are said to be isomorphous even when the elements in the isolated state do not exhibit any similarity of crystalline form. The replacement always takes place in stœchiometric quantities, so that a certain quantity of one element replaces or is replaced by a definite quantity of another, its crystallographic equivalent, while the other constituents of the compound remain unchanged. Isomorphous compounds have the power of crystallising together in such a way that they form homogeneous crystals independently of the proportions in which they are mixed. The alums, the vitriols and their double salts, the phosphates and arsenates are well-known examples of groups of isomorphous compounds.

Unfortunately no element has yet been discovered which is isomorphous with hydrogen, so that the crystallographic equivalents of the other elements cannot be directly compared with hydrogen, the usual standard. But by starting with the equivalent weight of an element which has been determined by one of the other methods, we can ascertain the crystallographic equivalents of any other elements of the same isomorphic group. If any members of this group exhibit isomorphism with other elements we can go on step by step until the equivalents of a large number of elements have thus been determined. Potassium is isomorphous with rubidium, cæsium, and thallium. The equivalent weight of potassium 39·03 (§ 11) is isomorphously replaced by 85·2 parts by weight of rubidium, 132·7 of cæsium, and in many compounds by 203·7 parts of thallium. This last quantity is isomorphous with 113·6 parts of indium.

Whether sodium is, strictly speaking, isomorphous with potassium is still doubtful; many analogous compounds of these two elements certainly exhibit identical crystalline forms, but as a rule they do not crystallise together. If we are justified in regarding the instances of identity of crystalline form as cases of isomorphism, then 39·03 parts by weight of potassium are equivalent to 23 parts of sodium, and these are equivalent to 7·01 parts of lithium and 107·66 of silver.

But the equivalent of silver can be replaced isomorphously by 63·18 parts by weight of copper, and the latter metal is a member of the group of metals forming vitriols and can be isomorphously replaced by—

58·69 parts by weight of nickel
58·99 ,, cobalt
55·88 ,, iron

54·8	parts by weight of	manganese
65·1	„	zinc
24·3	„	magnesium

The four last elements are isomorphous with 39·91 parts of calcium, and iron is isomorphous with 27·04 parts of aluminium and 52·0 parts by weight of chromium.

Calcium is also isomorphous with 87·3 parts of strontium, 136·9 parts of barium, and 206·4 of lead.

In some compounds zinc can be replaced by 111·8 parts of cadmium. The highest oxides of chromium and manganese enable us to pass on to the non-metals and semi-metals. For the chromates and manganates have the same crystalline form as the sulphates, selenates, tellurates, molybdates, and tungstates, and the permanganates have the same crystalline form as the perchlorates. The isomorphism of these salts provides us with the following crystallographic equivalent weights :—

31·98	parts of	sulphur
78·87	„	selenium
125·0	„	tellurium
95·9	„	molybdenum
183·6	„	tungsten
35·37	„	chlorine

Further 79·76 parts of bromine, 126·53 parts of iodine, and probably 19·06 of fluorine are isomorphous with 35·37 parts by weight of chlorine.

There are several other large groups of isomorphous elements. The phosphates, vanadates, and arsenates are isomorphous, and there are instances of isomorphism in the oxides of arsenic, antimony, and bismuth, which can with difficulty be brought into relation with the preceding elements. In the free state arsenic is isomorphous with antimony, bismuth, and tellurium. But it is obvious that the crystallographic equivalent can only be deduced from the isomorphism of the compounds, and not from the isomorphism of the free elements, for in the latter case there are no means of ascertaining what weight of the one element can replace a given weight of the other.

It is assumed in certain minerals that sulphur and tellurium are isomorphously replaced by arsenic and antimony; if this is really the case then we have the following crystallographic equivalents:—

30·96	parts by weight of	phosphorus
74·9	,,	arsenic
208·9	,,	bismuth
51·1	,,	vanadium
119·6	,,	antimony

Silicon, titanium, zirconium, thorium, and tin form another isomorphous group, and tin is related to the isomorphous group of the platinum metals containing platinum, iridium, osmium, palladium, rhodium, and ruthenium; these two groups are thus brought into relation with each other, and the following equivalents are obtained:—

28·33	parts by weight of	silicon
48·01	,,	titanium
90·4	,,	zirconium
232·0	,,	thorium
118·8	,,	tin
194·3	,,	platinum
192·5	,,	iridium
190·3	,,	osmium
106·3	,,	palladium
102·7	,,	rhodium
101·4	,,	ruthenium

If the isomorphism of titanium and iron be admitted, on which there is still some doubt, this group may thus be brought into relationship with the iron group. Some of the crystallographic equivalent weights arrived at in this way may not be correct, for doubtless some of the cases of isomorphism may prove not to be genuine. But the great advantage of this method is that it can only give one equivalent weight for each element, whereas the other methods may yield two or more equivalent weights.

After the discovery of the law of isomorphism Berzelius regarded the crystallographic equivalent weights as identical with the atomic weights, except in the case of K, Na, Li, Ag, of which he determined the atomic weights by the use of their electrolytic equivalents. The identification of the crystallographic equivalents with the atomic weights offered a lucid explanation of the phenomena of isomorphism. Imagine that a crystal is a regular structure composed of small particles of matter, called molecules, the molecules being themselves systematically built up of a definite number of atoms. If in each of these particles one atom is replaced by another of similar shape and size it is clear that the whole structure will remain unaltered in shape and arrangement. This is obvious, for experience shows us that, although the crystallographic equivalents vary considerably in weight, they all occupy approximately the same space.

We are, however, acquainted with a series of cases in which it is apparently not permissible to assume that replacement takes place atom for atom. In innumerable compounds the equivalent of potassium (39·03) is isomorphously replaced by 14·01 parts of nitrogen and 4 parts of hydrogen, and scarcely the slightest difference between the two classes of compounds is to be found. Consequently since Mitscherlich's first discoveries it has been assumed that an atom of potassium can be isomorphously replaced by the 'compound radical' ammonium ($NH_4 = 18{\cdot}01$), composed of one atom of nitrogen ($N = 14{\cdot}01$) and four atoms of hydrogen. But if this is possible in one case, it may frequently happen that several atoms replace one single atom. If we admit this, then the foundation of these considerations is weakened.

Another weak point in determining atomic weights by isomorphism is that many elements must be omitted, and hydrogen amongst the number. As a natural consequence the atomic weights can only be referred to the unit by making certain arbitrary assumptions. In fact we have already started with the arbitrary assumption that the equivalent weight of potassium as compared with hydrogen is 39·03. If we had taken it as half, or, like Berzelius, as double this value, we should have obtained for all the other elements values half or double their present atomic weights, and it would not have been possible to prove that these values were incorrect.

§ 14. **Thermic Equivalents.**—In 1819, at the time when Mitscherlich discovered the law of isomorphism, two French chemists, Dulong and Petit, observed the existence of another simple relation between the chemical combining weights of the elements and a physical property, viz. their specific heat or capacity for heat in the solid state. The atomic weights are approximately inversely proportional to the specific heats, and consequently the product of these two values is nearly the same for all elements. In order to make this law valid Dulong and Petit found it necessary to alter the accepted combining weights of some of the elements. Although these changes were not at the time generally welcomed, they are now universally adopted (except in the case of a few small errors), and all the more recent specific heat determinations have confirmed the accuracy of the law of Dulong and Petit. This important law is of general application. It gives the same values as the law of isomorphism and meets with the same difficulty, for here again the results cannot be directly referred to hydrogen as the standard, for solid hydrogen has not yet been investigated. If we take any of the crystallographic equivalents mentioned in the preceding paragraph, and multiply each by the specific heat of the element, we obtain approximately the same product.

The explanation of this fact is very simple. As the specific heat is the amount of heat required to raise the unit weight of a substance from 0° to 1° C. this product represents the amount of heat required to raise the equivalent weight by 1° C. The weight of the given element, which is heated 1° C., is termed the thermic equivalent weight. If we regard this as the atomic weight, then the product of the atomic weight into the specific heat is the atomic heat, *i.e.* the amount of heat taken up by one atom. It is clear that the atoms of the different elements have the same capacity for heat. The law may be simply expressed by saying that the atomic heats of all the elements are approximately equal.

This law applies without exception to all the malleable

Element	Specific Heat c	Atomic Weight A	Atomic Heat $A . c$
Lithium	0·941	7·01	6·6
Sodium	0·293	23·00	6·7
Magnesium	0·250	24·3	6·1
Aluminium[1]	0·214	27·0	5·8
Phosphorus	0·174	30·96	5·4
Sulphur	0·178	31·98	5·7
Potassium	0·166	39·03	6·5
Calcium	0·170	39·91	6·8
Titanium	0·129	48·0	6·2
Chromium	0·121	52·0	6·3
Manganese	0·122	54·8	6·7
Iron	0·114	55·88	6·4
Cobalt[2]	0·107	58·9	6·3
Nickel[2]	0·108	58·69	6·3
Copper	0·095	63·18	6·0
Zinc	0·094	65·1	6·1
Gallium	0·079	69·9	5·5
Germanium	0·077	72·3	5·6
Arsenic	0·081	74·9	6·1
Selenium	0·076	78·87	6·0
Bromine	0·084	79·76	6·7
Zirconium	0·066	90·4	6·0
Molybdenum	0·072	95·9	6·9
Ruthenium	0·061	101·4	6·2
Rhodium	0·058	102·7	6·0
Palladium	0·059	106·35	6·3
Silver	0·057	107·66	6·1
Cadmium	0·054	111·8	6·0
Indium	0·057	113·6	6·5
Tin	0·055	118·8	6·5
Antimony	0·051	119·6	6·1
Tellurium	0·048	125·0	6·0
Iodine	0·054	126·54	6·8
Lanthanum	0·045	138·0	6·2
Cerium	0·045	139·9	6·3
Tungsten	0·033	183·6	6·1
Osmium	0·031	190·3	6·1
Iridium	0·032	192·5	6·3
Platinum	0·032	194·3	6·3
Gold	0·032	196·7	6·4
Mercury	0·032	199·8	6·4
Thallium	0·033	203·7	6·8
Lead	0·031	206·4	6·4
Bismuth	0·030	208·9	6·3
Thorium	0·028	231·9	6·4
Uranium	0·028	238·8	6·6

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[1] Thomsen (*Zeitschr. f. anorg. Chem.* 15,447) has deduced the value 26·77 for the atomic weight of aluminium, hydrogen being the unit.

[2] The atomic weights of cobalt and nickel have been re-determined by Richards and Baxter and also by Richards and Cushman, and the values Co = 58·55 and Ni = 58·25 have been deduced. (*Proc. Amer. Acad.* 23,115, and 23,97.)

metals, to almost all the brittle metals, and to the majority of the non-metals. The table on p. 23 contains in the first column the names of the elements, in the second column under c the specific heats, in the third the thermic equivalent or thermic atomic weight A, and in the fourth the product $A \cdot c$, the atomic heat. The specific heat of most of the elements has been determined between the boiling point of water and the mean temperature of the atmosphere, but in the case of easily fusible elements the determinations are made at temperatures below their melting points, as most bodies exhibit abnormal specific heats at a temperature near their melting point.

The atomic heats in the above table do not exhibit absolute uniformity—the values vary between 5·4 and 6·9. The thermic equivalent or atom may now be defined as that stœchiometric quantity which on multiplication by the specific heat yields a constant which is approximately 6. If the specific heat of ice is taken as the unit, or the equivalent weight of some other element instead of hydrogen is taken as the standard, then different values are obtained. If the atomic weight of oxygen is taken as 100, then the atomic heats vary between 38 and 40.

As the atomic heat is almost constant, and as

$$A \cdot c = \text{const.} = 6{\cdot}3 \text{ approximately,}$$

it is clear that the value of A or c can be calculated approximately if one of these values is known.

§ 15. **Exceptions.**—In attempting to calculate the thermic equivalents of the elements by this method, we occasionally obtain values which cannot represent the true atomic weights. Regnault found for pure carbon in the form of diamond the specific heat $c = 0{\cdot}147$, and for graphite, another modification of the same element, $c = 0{\cdot}198$. The chemical equivalent of carbon is in § 11 stated to be 2·9925. The atomic weight must either be 2·9925 or a simple multiple of this number.

If $a = 2{\cdot}9925$, then $A = n \cdot a$, where n is a whole number and $c \cdot A = c \cdot n \cdot a = 6{\cdot}3$ approximately.

Let $n = 1 . 2 . 3$, &c.; then we have for

Diamond		*Graphite*	
n	$n . a . c$	n	$n . a . c$
1	0·44	1	0·59
2	0·88	2	1·18
.	.	.	.
10	4·40	10	5·92
11	4·84	11	6·52
12	5·28	12	7·11
13	5·72	13	—
14	6·12	14	—

The atomic weight of carbon, calculated from the specific heat of the diamond, would be

$$13 . a = 38{\cdot}90 ; \text{ or } 14 . a = 41{\cdot}89.$$

But if it is deduced from the specific heat of graphite, then

$$10 . a = 29{\cdot}92 ; \text{ or } 11 . a = 32{\cdot}92.$$

Even if we disregard the want of agreement between these results, such atomic weights would lead to monstrous formulæ for the numerous compounds of carbon, and on this ground alone they could not be accepted.

Carbon forms the most pronounced exception to the law. Boron, silicon, and beryllium also form exceptions, and the values for phosphorus and sulphur do not agree closely with the atomic heats of the other elements.

It is a well-known fact that the specific heat, and therefore the atomic heat, is different at different temperatures. A careful comparison of all the determinations of specific heats led H. F. Weber to the conclusion that the influence of temperature on the specific heats of those elements which form exceptions to the law is so great that they would follow the law at temperatures above 100°. Weber proved by experiment this hypothesis to be correct in the case of carbon, silicon, and boron. Nilson, Pettersson, and Humpidge have recently proved the same for beryllium. The specific heats of these elements increase with the temperature, at first rapidly, afterwards more slowly, until they become almost constant at high temperatures. The values obtained at high temperatures agree fairly well with the law of Dulong and Petit. The smallest stœchiometric quantities (equivalent to one part by weight of hydrogen) of these four elements are—carbon 2·99, boron 3·63, silicon 7·08, and beryllium 4·55. The atomic weights must be simple multiples of these numbers.

In the following table *c* gives the specific heats at high temperatures, A the atomic weights, which on multiplication by the specific heats yield the atomic heats A . *c*.

—	*c*	A	A . *c*
Beryllium	0·621 at 500° C.	9·1	5·64
Boron	0·5 [1] „ 600°	10·9	5·5
Carbon	0·459 „ 980°	11·97	5·51
Silicon	0·203 „ 230°	28·3	5·74

These values of A obey the law of Dulong and Petit fairly well; but it is clear that this law would not have led to their adoption if they had not already been discovered by other methods.

All the elements which exhibit deviations from the law, their atomic heats being too low, have small atomic weights, and are, as a rule, non-metals. The law always applies to elements with atomic weights thirty-six or forty times that of hydrogen.

When in any case the specific heat yields a low atomic weight the result must be regarded as doubtful, and the specific heat should be determined at different temperatures, in order to see whether it varies considerably with the temperature.

§ 16. **Specific Heat of Atoms in Compounds.**—The law of Dulong and Petit also holds good for elements in the state of combination. The specific heat of a compound in the solid state is approximately equal to the sum of the specific heats of its constituents. In the case of silver iodide, for example, we have—

Silver . . $A . c = 107·66 \times 0·056 = 6·1$
Iodine . . $A . c = 126·54 \times 0·054 = \underline{6·8}$
Total 12·9

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[1] Calculated by interpolation from the observations. At 233° $c = 0·366$.

The specific heat of silver iodide (AgI) is $c = 0{\cdot}061$, if this value is multiplied by the sum of the atomic weights, then we obtain the capacity for heat of that quantity of the compound represented by the formula, AgI.

$$c\,(\mathrm{Ag} + \mathrm{I}) = 0{\cdot}061 \times (107{\cdot}66 + 126{\cdot}54) = 14{\cdot}3.$$

This is only a little greater than the sum of the specific heats of the constituents. In the same way in the case of silver bromide—

$$\begin{array}{rl}
\mathrm{Ag}\,.\,c = 107{\cdot}66 \times 0{\cdot}056 = & 6{\cdot}1 \\
\mathrm{Br}\,.\,c = 79{\cdot}76 \times 0{\cdot}084 = & \underline{6{\cdot}7} \\
\mathrm{Ag} + \mathrm{Br} = 187{\cdot}42 \qquad\qquad & 12{\cdot}8 \\
\text{and } (\mathrm{AgBr})c = 187{\cdot}42 \times 0{\cdot}074 = & 13{\cdot}9.
\end{array}$$

The stœchiometric quantities of these substances composed of two thermic equivalents or atoms, AgI and AgBr, require about thirteen units of heat to raise their temperature by 1°C., *i.e.* double as much as a single atom. Compounds containing three thermic atoms have a capacity for heat three times as great, namely, 3 × 6·4, *i.e.* 19 or 20. In the case of lead bromide and iodide—

$$\begin{array}{ll}
c\,.\,(\mathrm{Pb} + 2\mathrm{Br}) = 0{\cdot}0533 \times (206{\cdot}4 + 2 \times 79{\cdot}76) & = 19{\cdot}5 \\
c\,.\,(\mathrm{Pb} + 2\mathrm{I}) = 0{\cdot}0427 \times (206{\cdot}4 + 2 \times 126{\cdot}54) & = 19{\cdot}6
\end{array}$$

and the sum of the atomic heats of the elements are—

$$\begin{array}{c}
6{\cdot}4 + 2 \times 6{\cdot}7 = 19{\cdot}8 \\
6{\cdot}4 + 2 \times 6{\cdot}8 = 20{\cdot}0.
\end{array}$$

This fact is made use of to determine the thermic equivalents of those elements of which the specific heat cannot be directly determined. If the specific heats of iodine and bromine were unknown they could be approximately calculated from the preceding data.

35·37 parts by weight of chlorine unite with the thermic atomic weight of silver, Ag = 107·66, and form 143·03 parts by weight of silver chloride, 70·74 parts by weight of chlorine unite with one atom of lead, Pb = 206·4, to form 277·14 parts by weight of lead chloride. On multiplying these quantities by the corresponding values for the specific heats, the product is the capacity for heat of the stœchiometric quantity of the compounds ; deduct from this the atomic heat of the metals, and the remainder is the capacity for heat of chlorine.

$$\begin{array}{lr} c\,.\,143{\cdot}03 = 0{\cdot}091 \times 143{\cdot}03 = & 13{\cdot}0 \\ c\,.\,\mathrm{Ag} \qquad = 0{\cdot}056 \times 107{\cdot}66 = & 6{\cdot}1 \\ \hline \end{array}$$

Capacity for heat of 35·37 parts by weight of chlorine 6·9

$$\begin{array}{lr} c\,.\,277{\cdot}1 = 0{\cdot}066 \times 277{\cdot}1 = & 18{\cdot}3 \\ c\,.\,\mathrm{Pb} \qquad = 0{\cdot}031 \times 206{\cdot}4 = & 6{\cdot}4 \\ \hline \end{array}$$

Capacity for heat of 70·74 parts by weight of chlorine 11·9

Consequently the thermic equivalent of chlorine = 35·37, and the quantity which is attached to one atom of lead is twice this amount and represents two atoms, as the capacity for heat is nearly equal to twice 6 units. The thermic equivalent or atomic weight of an element can be deduced by means of the specific heat of its compounds, even when the atomic heats of the elements united with it are unknown, provided these elements form an analogous compound with an element of known atomic heat. For example :—

11·97 parts by weight of carbon
and 47·88 „ oxygen

unite with the thermic equivalent of lead = 206·4 to form 266·25 parts by weight of cerussite. This mineral has the specific heat $c = 0{\cdot}080$ and the capacity

$$0{\cdot}080 \times 266{\cdot}25 = 21{\cdot}3.$$

The following metals unite with the same quantities of carbon and oxygen :—

136·9 parts of barium forming 196·75 parts by weight of witherite $c = 0{\cdot}109$;

87·3 parts of strontium forming 147·05 parts by weight of strontianite $c = 0{\cdot}145$;

39·9 parts of calcium forming 99·75 parts by weight of arragonite $c = 0{\cdot}206$.

These quantities have, according to F. Neumann's discovery, the same capacity for heat as cerussite.

Witherite . . .	196·75 × 0·109 = 21·4
Strontianite . .	147·05 × 0·145 = 21·3
Arragonite . . .	99·75 × 0·206 = 20·6

From this we conclude that the amount of each metal contained in these compounds represents the thermic equivalents. Bunsen has proved this to be true by experiment in the case of calcium.

In this way the thermic equivalents of several elements have been arrived at which could not be determined directly, and do not on this account appear in the table on page 23, viz.

Chlorine	Cl = 35·37
Rubidium	Ru = 85·2
Strontium	Sr = 87·3
Barium	Ba = 136·9

But still the elements mentioned in § 15 remain exceptions, as the capacity for heat of their compounds is smaller than the value calculated from the number of their constituent atoms. This is also true of nitrogen, fluorine, oxygen, and hydrogen.

§ 17. **Relation between Atomic Weight and Vapour Density.**—As by chemical methods alone it was found impossible to fix the value of the atomic weights, other physical methods than the crystalline form and specific heat were soon employed. The most important of these is the law of combining volumes discovered by Gay Lussac and Alexander von Humboldt at the beginning of the present century. According to this law a simple relation exists between the volumes of the different gases (measured under similar conditions of temperature and pressure) entering into combination or mutually decomposing each other.

The densities of the gaseous elements at the ordinary temperature compared with air or hydrogen are as follows:—

	Air = 1	Hydrogen = 1
Hydrogen . . .	0·06926	1·00
Oxygen . . .	1·10563	15·96
Nitrogen . . .	0·9713	14·02
Chlorine . . .	2·450	35·37

These elements unite together in the following proportions:—

	By Volume	By Weight
Hydrogen and chlorine	1 : 1	1 : 35·37
„ „ oxygen	2 : 1	1 : 7·98 =2 : 15·96
„ „ nitrogen	3 : 1	1 : 4·67 =3 : 14·01
Oxygen „ „	1 : 1	1 : 0·878=15·96 : 14·01
„ „ „	1 : 2	1 : 1·756=15·96 : 28·02
„ „ „	2 : 1	1 : 0·439=31·92 : 14·01

The combining weights of the gaseous elements are either directly proportional to their densities or to a simple multiple of their densities. The simplest hypothesis is that the atomic weights are proportional to the densities, *i.e.* to the weight of equal volumes of the gases. That is to say, that under similar conditions of temperature and pressure equal volumes of the different gaseous elements contain the same number of atoms. Berzelius made this assumption, the validity of which was contested by Dalton. When this law was applied to elements which only assume the gaseous state at high temperatures the following results were obtained:—

	Air = 1	Hydrogen = 1
Sulphur	6·62	95·94
Phosphorus	4·35	62·8
Arsenic	10·4	150·2
Mercury	6·93	100

In these cases the densities compared with hydrogen cannot be regarded as the atomic weights; for the numerous analogies between oxygen and sulphur show that the atomic weight of the latter is almost exactly double that of the former, *i.e.* 31·98, not 95·94. The close analogy between the compounds of nitrogen and those of phosphorus and arsenic indicate that if N=14·0, then P=30·36 and As=74·9; that is, the atomic weights are, in the case of phosphorus and arsenic, only half the densities; for only in the latter case will the corresponding hydrides have the analogous formulæ, NH_3 PH_3 and AsH_3; if the atomic weights are doubled the two latter must be represented by the formulæ PH_6 and AsH_6. There are also good grounds for doubting that the atom of mercury is only 100 times as heavy as the atom of hydrogen; consequently Berzelius was obliged to regard it as 200 times the weight of a hydrogen atom. The same is true of other atomic weights deduced from the density in the gaseous state; but some atomic weights arrived at by this method, *e.g.* those of iodine and bromine, agree with the results obtained for chlorine and others in the first group of elements.

§ 18. **Want of Agreement between the different Equivalents.** The different methods used in determining the equivalent weights of the elements led to different results. The atomic weights deduced by the chemical, electrolytic, crystallographic or thermic methods occasionally agreed and occasionally disagreed. It is not surprising, therefore, that there was a great want of unanimity in the views which chemists held concerning these fundamental values.

In spite of great difficulties, Berzelius understood how to make use of first one and then another of these physical auxiliaries and with such success that, with a few exceptions, the atomic weights he proposed are in use at the present day, although they were for a time replaced by the values proposed by Leopold Gmelin, which were based on Dalton's results. It is true the victory of the atomic weights of Berzelius was not won by himself, but, strange to say, to a great extent by his most active opponents, whose views he strongly disputed.

The result of this long and involved discussion was to clear and strengthen our views. In the present day a difference of opinion may exist for a time regarding an element which has not been thoroughly investigated, but no dispute can arise on the fundamental principles involved in the determination of atomic weights. These principles were first clearly explained by S. Cannizzaro in 1858, when the apparent contradictions between certain results were satisfactorily cleared away.

§ 19. **Avogadro's Hypothesis.**—Cannizzaro was the first to point out that an entirely false construction had been placed on the relation which exists between the density of a gas or vapour and the combining weight, in spite of the fact that in 1811 Amadeus Avogadro had given perfectly correct instructions as to the manner in which this relationship was to be employed. Starting from Gay Lussac's recently discovered law of combining volumes, Avogadro enunciated the hypothesis that under similar conditions of temperature and pressure, equal volumes of gases contain the same number of particles, which need not of necessity be atoms. He called these particles 'molecules,' from *molecula*, a small mass (*moles*).

Although Avogadro's hypothesis was not the only one possible, it was by far the most probable. Nevertheless for a long time it failed to meet with approval, and the views held by chemists were in many ways directly opposed to it. For example, for half a century no one opposed the views held by Dalton and Gmelin, that water contains one atom of oxygen and one atom of hydrogen, although as a necessary consequence it follows that a given volume of oxygen must contain twice as many atoms as the same volume of hydrogen.

If each particle of water contains the same number of atoms of each constituent, then one volume of oxygen must contain the same number of atoms as are contained in two volumes of hydrogen. For two volumes of hydrogen unite with one volume of oxygen to form water.

The chief reason why Avogadro's hypothesis failed to meet with recognition was that at this time there was no real necessity for applying it (as Avogadro had done) not only to the elements but to their compounds. At this period only a few gaseous compounds were known, and little importance was attached to the manner in which their chemical formulæ were written. About the middle of the present century the necessity for a systematic classification of the numerous newly discovered carbon compounds, the so-called organic compounds, made itself felt. Avogadro's hypothesis, which had so long lain dormant, was admirably adapted for this purpose. At first its application was partial and limited, until C. Gerhardt made a logical use of it and then mainly with the object of classifying chemical compounds.

§ 20. **Physical Basis of Avogadro's Hypothesis. The Kinetic Theory of Gases.**—Avogadro had pointed out the extraordinary similarity in the physical properties of different gases, more particularly the uniformity exhibited by the influence of temperature and pressure on their volume and density, as stated in Boyle's or Mariotte's law and in Gay Lussac's law. He was of opinion that the only possible explanation lay in the hypothesis that all gases contain the same number of particles in equal volumes, measured under similar conditions of temperature and pressure. For if one gas contained double or treble the number of particles contained in another, it would be almost impossible to understand how the relations between density, temperature, and pressure could agree under these conditions: but it is obvious that if the same number of particles of different gases are contained in equal volumes, then the same change in pressure will be effected if the volume is increased or diminished to a certain extent or the temperature altered by a certain number of degrees.

This idea of Avogadro has received decisive confirmation as a result of the new development of the mechanical theory of heat. This theory starts from an old hypothesis which was developed by Daniel Bernouilli in 1738. According to this theory, the individual particles of matter in the solid state occupy definite positions with regard to each other. In the liquid state, although the particles have the power of moving about freely they are attracted to each other; but in the gaseous state the particles are entirely detached from each other: each particle moves about with great rapidity and rushes forward in a straight line until it comes in contact with another particle or some other impediment, from which it rebounds like an elastic ball and continues its movement in a new direction. The pressure of a gas results from the sum of the impacts which the particles exert on the body they come in contact with—the sides of a vessel, for example. Consequently the pressure increases, as the number of particles in a given space and as the velocity of the particles increases.

This old hypothesis was rediscovered in 1850 by Krönig, Joule, and Clausius, and received a more systematic development at the hands of Clausius. It forms the basis of the theory known as the theory of starting molecules or the kinetic theory of gases. According to this theory the pressure exerted by a given volume of gas is proportional to the sum of the kinetic energy of the rectilinear motion of all the particles contained in the unit of volume. By kinetic energy we understand half the product of the mass into the square of the velocity. The pressure of the gas is proportional to the sum of the products obtained by multiplying the mass of each individual particle by half the square of its velocity. And as, according to Gay Lussac's law, the pressure varies in proportion to the temperature, it follows that the sum of these products is also proportional to the temperature, and consequently for constant mass the temperature is proportional to the square of the velocity.

If we have equal volumes of two different gases at the same temperature and under the same pressure, then the total kinetic energy is the same in each volume. But according to Avogadro's hypothesis the number of particles in both gases is identical; consequently the average kinetic energy of each individual particle will be the same. If the two gases are brought into communication with each other, they mix together without any change of temperature or pressure taking place, providing of course that the gases do not exert any chemical action on each other. In this mixture, again, every particle will have the same kinetic energy.

Without the aid of Avogadro's hypothesis, we are at once surrounded by difficulties. Let us assume that one gas contains twice as many particles in a certain volume as another gas, then each particle of the first gas has only half the kinetic energy of the particles of the second, for the total kinetic energy is shared by double the number of particles. By the laws of mechanics, it is impossible that this condition should continue when the gases are mixed together; and as the particles are frequently coming into collision with each other, those doubly endowed with kinetic energy must give up a portion of their energy to the other particles. But if this transference of energy takes place, then the two gases will cease to be under the same temperature and pressure, because temperature and pressure are proportional to the kinetic energy of the gases. Avogadro's hypothesis is the only means of arriving at results conforming to the laws of mechanics.

This is one of the most powerful arguments in support of Avogadro's hypothesis, its truth is now no longer disputed.

§ 21. **Molecular Weights of Gases.**—The relative values for the molecular weights of all gases can be easily determined by means of Avogadro's hypothesis. The absolute weight of the molecules cannot be ascertained. The method depends on the fact that the weight W of a given volume of gas is equal to the sum of the weights of all the separate particles contained in it; so that

$$W = n \,.\, m,$$

where n represents the number of particles and m the weight of a single particle, *i.e.* the 'molecular weight.'

For a second gas

$$W' = n' \,.\, m'.$$

In these equations, n, n' and m, m' are unknown values, but the weights W and W′ can be determined by experiment.

By comparing quantities of two gases which occupy equal volumes under similar conditions of temperature and pressure we have according to the hypothesis $n = n'$, and

$$W : m = W' : m' ;$$
$$m' : m = W' : W.$$

The relative values of the molecular weights can be easily calculated from the weights of equal volumes of the two gases as ascertained by experiment. If the unit of volume is 1 litre = 1 cubic decimetre, or even a cubic centimetre, then the weights W and W′ indicate the weight of the unit volume, or the densities d and d'.

The equation

$$m' : m = d' : d$$

signifies that the molecular weights of different gases bear the same ratio to each other as do their densities, if the latter are determined at the same temperature and pressure.

The particular standard used in measuring densities is immaterial, although it is customary as well as convenient to use as the standard of comparison dry hydrogen or dry atmospheric air free from carbon dioxide. It is always understood that the comparison between a given gas and the standard is made under similar conditions of temperature and pressure. With this assumption the above law may be briefly formulated thus: the molecular weights of gases are proportional to their densities.

§ 22. **Unit of Molecular Weights.**—The same reasons which led to the adoption of the atom of hydrogen as the unit of atomic weights caused hydrogen to be chosen as the standard of molecular weights. At first sight it would seem best to take the molecule of hydrogen=1 and compare the molecular weights of all other gases with this unit, *i.e.* represent their molecular weights by numbers indicating how many times heavier they are than hydrogen. This is certainly permissible, but it is much more convenient to compare the weights of the molecules, which are composed of atoms, with the same standard by which the atomic weights were measured, so that the molecular weights may be directly represented as the sum of the atomic weights. In order to do this it is necessary to know what relation the molecular weight of hydrogen bears to its atomic weight. The molecular weight cannot be smaller, but it may be larger than the atomic weight, as the molecule may contain several atoms. We are compelled to assume that it contains more than one atom, as gaseous hydrogen compounds are known which only contain half as much hydrogen as is contained in the same volume of free hydrogen.

As one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid, it follows, from Avogadro's law, that each particle of hydrogen and chlorine produces two particles or molecules of hydrochloric acid, as the two volumes of the latter gas contain, according to this hypothesis, twice as many particles as are contained in one volume of one of its constituents. And as a particle of hydrogen and a particle of chlorine can divide into two parts, it must consist of at least two atoms. It cannot contain less than two, but it may contain more; but there is no reason for assuming the existence of more than two atoms in the molecule until a compound is discovered which contains less than half its volume of hydrogen.

The molecular weight of hydrogen is represented by

$$\mathfrak{H} = 2H = H_2 = 2.$$

§ 23. **Calculation of Molecular Weights.**—When the unit is chosen the calculation of the molecular weight of any other gaseous substance is extremely simple; for, according to § 21,

$$m : m' = d : d';$$

$$m = \frac{m' \,.\, d}{d'};$$

and

$$m' = \mathrm{H}_2 = 2,\ d' = 0{\cdot}06926;$$

$$m = \frac{2 \,.\, d}{0{\cdot}06926} = 28{\cdot}876 \ .\ d.$$

The molecular weight of any gas is calculated by multiplying its density compared with air at the same temperature and pressure by 28·876.

The relation is even more simple when the density is expressed in terms of hydrogen instead of air:—

$$m' = \mathrm{H}_2 = 2 \text{ and } \delta' = 1;$$

and

$$m = 2 \,.\, \delta.$$

This calculation yields the same results as the previous one, for the densities compared with air d are to the densities compared with hydrogen δ, as

$$d : d' = \delta : \delta';$$
$$d : 0{\cdot}06926 = \delta : 1;$$
$$d = 0{\cdot}06926 \times \delta;$$
$$\delta = 14{\cdot}438 \times d.$$

The densities of gases would no doubt be directly compared with that of hydrogen if it were not for the great experimental difficulties involved. This is the reason why the comparison with air is, as a rule, preferred.

The factors 14·438 and 28·876 in the preceding formulæ have a very simple meaning. The first number represents the specific gravity or density of dry atmospheric air in terms of hydrogen; the second number, which is double the first, represents the mean value of the molecular weights of its constituents. In the case of

Oxygen . $d = 1{\cdot}10563$, $\delta = 15{\cdot}963$, $m = 31{\cdot}93$.
Nitrogen $d = 0{\cdot}97137$, $\delta = 14{\cdot}025$, $m = 28{\cdot}05$.

But according to Bunsen, 100 volumes of air contain

Oxygen	20·96 volumes
Nitrogen[1]	79·04 „

Now, according to Avogadro's hypothesis, equal volumes of the two gases contain the same number of particles ; therefore, 10,000 particles of air contain

2096	particles of oxygen ;
7904	„ nitrogen.

But as oxygen is heavier than nitrogen, the average weight of a particle of air is

$$m = \frac{2096 \times 31 \cdot 93 + 7904 \times 28 \cdot 05}{10000} = 28 \cdot 86.$$

This result closely agrees with the value 28·876. This number has no real meaning, because no existing particle of air has this weight ; but it may be conveniently used in molecular weight calculations, as the molecular weight of any given gas bears the same relation to this value as the density expressed in terms of air does to 1.

§ 24. **Correction for Errors of Experiment.**—The molecular weights calculated by either of these methods generally require correction. The determination of the densities of gases and vapours, like all other observations, are liable to errors of experiment, which in some cases are considerable. Another point to be noticed is, that the expansion of different gases by heat, and the relation of their volume to pressure, is almost but not absolutely identical.

Hence it follows that if two gases exactly conform to Avogadro's law at a certain temperature and pressure, they will no longer do so at any other temperature and pressure, as both gases will not change their volume to absolutely the same extent. Since the deviations are but small, we may use the method mentioned in the preceding paragraphs, in order to make a fairly accurate determination of the molecular weights, and then correct the values so obtained. The correction is effected by making use of the fact that each molecule is composed of atoms; its weight must consequently be equal to the sum of the weight of the atoms contained in it.

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[1] Rayleigh and Ramsay showed in 1894 that 'atmospheric' nitrogen contains $\frac{1}{84}$ of its volume of argon, density 19·82.

The density of hydrochloric acid gas is found by experiment to be 1·247. Analysis proves that this gas contains 35·37 parts by weight of chlorine to 1 part by weight of hydrogen; therefore the molecular weight of this compound must either be $m = 1 + 35{\cdot}37 = 36{\cdot}37$, or a simple multiple of this number, as less than a whole atom of hydrogen ($=1$) cannot be present in the compound, The product of the density by 28·87 is $d \times 28{\cdot}87 = 1{\cdot}247 \times 28{\cdot}87 = 36{\cdot}0$, which agrees with the value calculated from the atomic weights; the difference is due to errors of experiment, and 36·37 must be held to be the correct molecular weight.

Marsh gas contains 2·9925 parts by weight of carbon to 1 part by weight of hydrogen. The molecular weight must be represented as

$$m = n\,(1 + 2{\cdot}9925) = n \times 3{\cdot}9925,$$

in which n stands for a whole number (possibly $n = 1$). The density compared with air $= 0{\cdot}555$, and the molecular weight will be approximately

$$m' = 28{\cdot}87 \times 0{\cdot}555 = 16{\cdot}02.$$

This is roughly four times the smallest value possible; consequently the true value is

$$m = 4 \times 3{\cdot}9925 = 15{\cdot}97 = (4 + 11{\cdot}97).$$

The molecular weight consists of 4 parts by weight of hydrogen and 11·97 parts by weight of carbon. In this way the molecular weights of numerous substances which can be volatilised without decomposition have been determined.

§ 25. **Determination of Atomic Weights from Molecular Weights.**—As the atoms are indivisible particles (*ἄτομοι*) a molecule cannot contain less than a whole atom. Hence the molecular weights of compounds offer special facilities for the determination of the atomic weights of the elements.

The smallest quantity of an element which is found to exist in the molecular weight of any of its compounds is the maximum value of the atomic weight. This smallest quantity must contain at least one atom; it may contain two, three, or more atoms. We are justified in regarding this smallest quantity as the atomic weight, if no good reasons exist for believing that this smallest quantity consists of more than one atom. We shall presently see that methods are not wanting which prevent the possibility of errors of this kind.

The table on the opposite page comprises a list of those substances which contain the smallest quantity of the given elements in the molecular weights of their compounds. The first column contains the names of the compounds; the second, under *d*, the density compared with air; the third, the corrected molecular weights calculated from the densities; the fourth, the amount of the element contained in the molecular weight; the fifth, the chemical equivalent; and finally, the sixth contains the thermic equivalent of the element, if the element be known in the solid state.

It is only in the case of a small number of elements that the chemical equivalent is identical with the atomic weight deduced from the molecular weight; as a rule, the chemical equivalent is a sub-multiple of the atomic weight, and is therefore entirely unsuited for the determination of atomic weights. The atomic weights coincide with the thermic equivalents and the latter agree with the crystallographic equivalents.

The smallest quantity of the element contained in the molecular weight of the compound is double the thermic equivalent only in the case of cuprous chloride. But even this case does not form an exception, if we assume that the molecule contains two atoms of copper. This shows that Cannizzaro was justified in the statement made in 1857 that the molecular weights can be determined by means of the vapour density and the atomic weights by the specific heat.

§ 26. **Possible Errors.**—It is obvious that the calculation of molecular weight from the density can only be made in the case of homogeneous gases. If it be attempted to apply this method to gaseous mixtures, the result obtained is only the mean value of all the molecular weights contained in the

Vapour Densities, Molecular and Atomic Weights

—	Density d	Molecular Weight m	Amount	Chemical Equivalent	Thermic Equivalent
Hydrofluoric acid	0·713	20·06	F: 19·06	19·06	19·06
Hydrochloric acid	1·260	36·37	Cl: 35·37	35·37	35·37
Hydrobromic acid	2·71	80·76	Br: 79·76	79·76	79·76
Hydriodic acid	4·443	127·54	I: 126·54	126·54	126·54
Water	0·623	17·96	O: 15·96	7·98	—
Sulphuretted hydrogen	1·191	33·98	S: 31·98	15·99	31·98
Selenium dioxide	4·03	110·8	Se: 78·87	39·43	78·87
Tellurium dichloride	6·9	195·7	Te: 125	62·5	125
Tellurium tetrachloride	9·22	266·5	Te: 125	62·5	125
Ammonia	0·597	17·01	N: 14·01	4·67	14·01
Nitric oxide	1·039	29·97	N: 14·01	4·67	14·01
Phosphine	1·15	33·96	P: 30·96	10·32	30·96
Phosphorous chloride	4·88	137·07	P: 30·96	10·32	30·96
Arsine	2·695	77·9	As: 74·9	24·97	74·9
Arsenic chloride	6·30	181·0	As: 74·9	24·97	74·9
Antimony trichloride	7·8	225·7	Sb: 119·6	39·87	119·6
Bismuth trichloride	11·35	315·0	Bi: 208·9	69·6	208·9
Stannic chloride	9·20	260·3	Sn: 118·8	29·7	118·8
Germanium chloride	7·44	213·8	Ge: 72·3	18·07	72·3
Thorium chloride	12·42	373·4	Th: 231·9	58·00	231·9
Zirconium chloride	8·15	231·9	Zr: 90·4	22·6	90·4
Titanium chloride	6·84	189·5	Ti: 48	12·0	48
Silicon chloride	5·94	169·8	Si: 28·3	7·07	28·3
Marsh gas	0·555	15·97	C: 11·97	2·99	11·97
Carbon monoxide	0·968	27·93	C: 11·97	2·99	11·97
Boron chloride	4·02	117·0	B: 10·9	3·63	10·9
Aluminium chloride	4·56	133·15	Al: 27·04	9·01	27·04
Indium chloride	7·39	219·7	In: 113·6	37·9	113·6
Gallium chloride	4·82	176·0	Ga: 69·9	23·3	69·9
Beryllium chloride	2·77	79·77	Be: 9·03	4·52	9·03
Thallium chloride	8·2	239·07	Tl: 203·7	203·7	203·7
Lead chloride	9·5	277·1	Pb: 206·4	103·2	206·4
Zinc chloride	4·57	135·84	Zn: 65·1	32·55	65·1
Cadmium bromide	9·25	271·0	Cd: 111·8	55·85	111·8
Mercuric chloride	9·8	270·5	Hg: 199·8	99·9	199·8
Chromium trichloride	5·47	158·1	Cr: 52	17·33	52·0
Ferric chloride	4·32	161·99	Fe: 55·88	27·94	55·88
Vanadium chloride	6·69	192·6	V: 51·1	12·8	—
Molybdenum chloride	9·46	272·7	Mo: 95·9	19·2	95·9
Tungsten pentachloride	12·7	360·4	W: 183·6	36·7	183·6
Tungsten hexachloride	13·2	395·8	W: 183·6	36·7	183·6
Uranium tetrachloride	13·33	380·3	U: 238·8	59·75	238·8
Niobium chloride	9·6	270·5	Nb: 93·7	19·74	—
Tantalum chloride	12·9	358·8	Ta: 182	36·4	—
Ruthenium tetroxide	5·77	163·3	Ru: 101·4	12·94	101·4
Osmium tetroxide	8·9	254·8	Os: 190·3	23·87	190·3
Cuprous chloride	7·05	197·1	Cu: 126·4	63·2	63·2

mixture (*vide* § 23). Mistaking such a mixture for a homogeneous gas may lead to grave errors.

The molecular weight calculated from the observed density of the vapour of ammonium chloride is

$$m' = d \times 28{\cdot}87 = 0{\cdot}89 \times 28{\cdot}87 = 25{\cdot}69,$$

which becomes after correction by the known combining weights of hydrogen, chlorine, and nitrogen:

$$m = 2 + 17{\cdot}685 + 7{\cdot}005 = 26{\cdot}69.$$

The quantities of chlorine and nitrogen (17·685 and 7·005 parts by weight respectively) are only half as large as the amounts found in the molecular weights of other compounds. If these quantities really do occur in the molecular weight of this compound, they must be regarded as the atomic weights of these elements, and we must assume that at least two atoms of these elements are contained in all their other compounds. But Pebal has shown that ammonium chloride splits up into equal volumes of ammonia and hydrochloric acid when it is converted into vapour. Its density is therefore the arithmetical mean of the densities of these two gases, and only one-half of the molecules present in the vapours contain chlorine; the other half contain nitrogen.[1] The densities of the constituents are

Ammonia	$d = 0{\cdot}59$
Hydrochloric acid	$d = 1{\cdot}25$
Mean	0·92

The molecular weights are

Ammonia . . .	$m = 14{\cdot}01 + 3 = 17{\cdot}01$
Hydrochloric acid . .	$m = 35{\cdot}37 + 1 = 36{\cdot}37$
Mean	26·69

Other ammonium salts, certain compounds of phosphorus, and other substances also exhibit abnormal vapour densities. These compounds cannot be used for molecular or atomic weight determinations.

On the other hand, if the vapour density is determined at too low a temperature the resulting molecular weight may be too high. Many substances when volatilised at the lowest possible temperature give a vapour the density of which, compared with air or other gases, is high, but at higher temperatures yield a relatively light vapour. If the vapour density is determined for a series of temperatures, it is found to decrease as the temperature rises until a point is reached above which it remains nearly constant. The chlorides of aluminium, gallium, and iron behave in this way. To explain this behaviour it is assumed that when these compounds are first converted into vapour they do not at once separate into isolated particles, but into aggregations of molecules, generally consisting of two molecules. These aggregations gradually break up as the temperature rises. Their dissolution may also be aided by reduction of pressure or by admixture with an indifferent gas.

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[1] *Translators' Note.*—Perfectly dry ammonium chloride does not dissociate. At the temperature of boiling mercury the vapour density is 26·8. H = 1. (H. B. Baker, *Chem. Soc. Jour.* 1894, 615; 1898, 425.)

§ 27. **Molecular Weights of the Elements.**—The molecular weights of the elements can be determined in the same way as the molecular weights of compounds. Some are identical with the thermic atomic weights, but as a rule they are larger than the latter. The following table gives a list of all the molecular weights of the elements known at the present time. The first column contains the names, the second the density in the state of gas or vapour at the temperature mentioned in the third column, the fourth the molecular weight calculated from the density and corrected by the results of analysis, and the fifth the atomic weight determined by Avogadro's (Av) or by Dulong and Petit's (DP) method.

Most of the elements contained in this table are either non-metals or semi-metals. Only a few of the metals are embraced in it, since, as a rule, they are difficult to volatilise; on the other hand, only a small number of non-metals are absent. There is a wonderful difference between the two groups; the semi-metals and non-metallic elements contain two or more atoms in the molecule; the molecules of the true metals only contain one atom.

It is probable that the ductility and other properties of the metals are in some way determined by this peculiarity.

I	II Density	III t	IV Molecular Weight	V Atomic Weight	VI
Hydrogen . .	0·06926	0° C.	H_2 = 2	H = 1	Av
Nitrogen . .	0·9714	0°	N_2 = 28·02	N = 14·01	Av
Oxygen . .	1·10563	0°	O_2 = 31·92	O = 15·96	Av
Fluorine . .	1·27	16°	F_2 = 38·12	F = 19·06	Av
Sulphur . .	2·24	940°	S_2 = 63·96	S = 31·98	Av DP
Zinc . . .	2·36	1400°	Zn_1 = 65·10	Zn = 65·10	Av DP
Chlorine . .	2·450	200°	Cl_2 = 70·74	Cl = 35·37	Av DP
Cadmium . .	3·94	940°	Cd_1 = 111·8	Cd = 111·8	Av DP
Phosphorus . .	4·35	500°	P_4 = 123·84	P = 30·96	Av DP
Bromine . .	5·54	100°	Br_2 = 159·52	Br = 79·76	Av DP
Selenium . .	5·68	1420°	Se_2 = 157·74	Se = 78·87	Av DP
Mercury . .	6·98	446°	Hg_1 = 199·8	Hg = 199·8	Av DP
Iodine . . .	8·72	940°	I_2 = 253·08	I = 126·54	Av DP
Tellurium . .	9·00	1440°	Te_2 = 250	Te = 125	Av DP
Arsenic . .	10·2	746°	As_4 = 299·6	As = 74·9	Av DP

The behaviour of sulphur is very remarkable. It has already been mentioned in § 17 that the vapour density at 500° is greater than at higher temperatures. This density corresponds to a molecular weight $S_6 = 191·88$, still it has not been decided with certainty whether the vapour of sulphur at a temperature a little above its boiling point (446° C.) is really composed entirely of hexatomic molecules. The density of the vapour changes as the temperature rises in a similar way to that exhibited by the compounds mentioned in § 26.

On the other hand the density of iodine (and in a lesser degree that of bromine and of chlorine) is abnormally low at very high temperatures. This is explained by assuming that some of the molecules are split up by the action of heat into individual atoms, and that as the temperature rises more molecules are split up.

The density of iodine vapour is

8·76 at 445°
7·01 „ 1043°
5·82 „ 1275°
5·06 „ 1470°

If the decomposition of the iodine molecules into atoms were complete, the original density would be halved. Bromine and chlorine exhibit similar peculiarities.

§ 28. **Nascent State.**—The necessity of assuming that the molecules of many elements contain two or more atoms has gradually made itself felt. This hypothesis has proved of great service in providing an explanation of certain apparently inexplicable phenomena. It has frequently been observed that many elements which, as a rule, do not readily enter into combination easily unite if brought together at the moment of their liberation from other compounds. In this specially active condition the elements are said to be in the 'nascent state.' The peculiar behaviour of elements in the nascent state is accounted for by assuming that they are then present as isolated atoms. Naturally these isolated atoms are more ready to enter into combination than they would be if they were already united to similar atoms in the form of molecules.

Hydrogen offers a striking example of the activity of elements in the nascent state. It is only at a high temperature that free hydrogen burns in oxygen, forming water, but both elements will unite at the ordinary temperature, or even at a lower temperature, at the moment of their liberation from other compounds. It is more difficult to combine free nitrogen with oxygen or hydrogen, but if the elements are in the nascent state combination readily takes place. It is easy to understand that isolated atoms at once unite when they meet each other, but when an atom is united to one or more atoms to form a molecule, it must first of all be detached from this molecule before it can form a new compound. The determination of molecular weights, and of the distinction between atoms and molecules, has been of the utmost importance to the extension of our views.

§ 29. **Determination of the Stœchiometric Values.**—Having considered the grounds on which the determination of the atomic weights is based, we must now proceed to the description of the methods employed in the exact determination of these highly important values. The process is far from simple. In the first place it is necessary to know, with the utmost degree of accuracy, the proportions by weight in which the given element unites with other elements. This knowledge can only be acquired by careful analyses or syntheses of compounds. But all our methods of analysis and synthesis are vitiated by certain errors, which can never be entirely avoided, but must be reduced to the narrowest limits. Those methods alone are to be used which can be carried out with the minimum amount of error. In analysis a certain definite weight of a compound is decomposed and the weight of its constituents determined. A distinction is made between partial and complete analyses, according as one or all the constituents are determined; and a similar distinction is drawn between partial and complete syntheses. When practicable, complete or total analyses or syntheses are preferred, as in these cases we have a guarantee that nothing has been lost or gained during the operations, when the sum of the weight of the constituents is equal to the weight of the compound. In many cases it is only possible to make a partial analysis or synthesis, as some substances cannot be brought into a form in which their weight can be ascertained with a sufficient degree of accuracy.

As to the means for determining the weight and therewith the mass of a body, the balance and weights have been developed to a point of such great accuracy that the error has been reduced to $\frac{1}{100000}$, or even $\frac{1}{1000000}$. But such accuracy can only be attained in weighing stable bodies, which occupy a very small space in proportion to their weight, and do not possess a very large surface; for large volumes and large surfaces increase the possible errors in weighing.

As weighings are generally made in atmospheric air, the substance weighed appears lighter than it really is by the weight of air it displaces. This loss of weight can be calculated and allowed for, but the error increases as the volume of air displaced increases. Air and other gases and moisture condense on the surfaces of the body weighed as well as of the vessels containing it, and in this way the error of weighing increases with the surface. This source of error can be diminished, but cannot be entirely avoided.

In atomic weight determinations we avoid, as far as possible, weighing gases or liquids, on account of the error introduced by the use of large vessels for holding them. This can be accomplished by measuring instead of weighing these bodies, if the weight of the unit of volume, *i.e.* the density, has been once determined.

The use of substances which easily oxidise, absorb moisture from the atmosphere, or in other ways change, should be avoided if possible; if it is necessary to employ them they must be weighed in air-tight vessels, which have either been exhausted by the air-pump or filled with an indifferent gas.

It frequently occurs that an element in the free state is unsuitable for weighing. In this case it is converted into a suitable compound, which is weighed, the amount of the element in the compound having been previously accurately determined. Chlorine is weighed as silver chloride, sulphur as barium sulphate, &c.

Great care must be taken to insure the purity of the substance investigated and of the other substances used in the various operations, in order that the bodies which are weighed may really have the composition they are supposed to possess. If these precautions are neglected very grave errors will follow.

§ 30. **Relation of Stœchiometric Determinations to each other.**—Since hydrogen has been selected as the unit of equivalent and atomic weights, it is desirable to compare all determinations with this standard. Unfortunately hydrogen only unites with about a dozen other elements, and these compounds are mostly gaseous like hydrogen, and consequently difficult to determine quantitatively. Berzelius determined the atomic weights of nearly all the elements with which he was acquainted with wonderful accuracy, using as his unit the hundredth part of an atom of oxygen, regarding the atomic weight of oxygen as 100. He did this instead of using Dalton's unit, hydrogen = 1, on account of the difficulty involved in accurately determining the composition of the gaseous compounds of hydrogen. He also occasionally made use of Dalton's unit, calculating out his results in terms of this standard. At the present day we are frequently compelled to adopt this indirect method. This indirect method involves the knowledge of the proportion by weight in which hydrogen and oxygen unite to form water, and as a natural consequence this determination has been made with the greatest care. The ratio 1 : 7·98 has been obtained as the mean of numerous concordant results arrived at by different methods. Water contains 1 part by weight of hydrogen to 7·98 of oxygen, and according to Avogadro's law (§ 19) we consider that water contains two atoms of hydrogen, but does not contain two or more atoms of oxygen.

Therefore

$$H_2 : O = 1 : 7{\cdot}98, \text{ or } H : O = 1 : 15{\cdot}96.^1$$

There may be an error of one or more units in the second place of decimals: that is, an error of some thousandths of the total value. The practice of representing the atomic weight of oxygen as a whole number, 16, is unwarrantable. Where great accuracy is not necessary the round number may be used as a matter of convenience, and the calculated result will be nearly accurate; but when scientific accuracy is required such arbitrary alterations in the experimental results are not permissible.

Having determined the atomic weight of oxygen in this way, we can now compare a large number of atomic weights of other elements, chiefly metals, with the atomic weight of hydrogen. The amount of oxygen in the oxides is determined by analysis or synthesis. The quantity of the element which unites with an atom of oxygen is equivalent to two atoms of hydrogen. Whether this quantity represents the atomic weight or a multiple or sub-multiple is ascertained by means of Avogadro's law, by the law of Dulong and Petit, or by isomorphism.

An example will explain the method. Berzelius obtained 4·2835 grams of oxide by oxidising 2·9993 grams of pure iron, or 1·42817 gram of oxide from 1 gram of iron, or making the necessary corrections for weighing in air 1·42836 gram of oxide from 1 gram of iron. One part by weight of the metal united with 0·42836 of oxygen. The quantity of metal A oxidised by one equivalent = 7·98 parts by weight of oxygen is

$$1 : A = 0{\cdot}42836 : 7{\cdot}98;$$
$$A = 18{\cdot}629.$$

This number cannot be the atomic weight of iron, for on multiplying it by the specific heat of the metal, $c = 0{\cdot}114$, it

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[1] Recent results give a slightly lower value for oxygen, viz. J. Thomsen, 15·869; E. W. Morley, 15·879 (1896).

yields the product $A \,.\, c = 2{\cdot}13$, whilst treble the value, *i.e.* 55·89, yields 6·4. The latter number also represents the quantity of iron contained in the molecular weight of ferric chloride (§ 25); this must therefore be regarded as the atomic weight of iron compared with hydrogen as unity. Similar determinations by other chemists yield almost identical results. The mean of the most trustworthy results gives 55·88 as the atomic weight of iron.

The oxides of many elements are difficult to prepare in a state of perfect purity. This is true of many of the light and of some of the noble metals, but the chlorides, bromides, &c. of these elements are admirably adapted for weighing. In such cases the comparison of the atomic weight with that of hydrogen is made by a more indirect method than the preceding. The compounds of silver with chlorine, bromine, and iodine are quite insoluble in water, and are therefore well adapted for analytical determinations. The proportions by weight with which these elements unite with silver have been very carefully estimated. In fact, the most correct of all the stœchiometrical determinations that have ever been made are those which fixed the combining proportions of silver and iodine—

$$Ag : I = 1 : 1{\cdot}17534.$$

This determination was carried out by Stas with the utmost care and skill; the experimental error is about 1 in 100,000. As oxide of silver is too unstable to permit of correct analysis the proportion of silver to oxygen had to be determined by several indirect methods, all of which have yielded similar results.

The analysis of potassium chlorate, $KClO_3$, gave the relative quantities of potassium chloride, KCl, and oxygen in the salt:

$$KCl : O = 4{\cdot}6616 : 1.$$

By converting weighed quantities of potassium chloride, KCl, into silver chloride, AgCl, the following ratio was obtained:

$$Ag : KCl = 1 : 0{\cdot}69104.$$

Hence it follows that

$$Ag : O = \frac{Ag}{KCl} \times \frac{KCl}{O} = \frac{4 \cdot 6616}{0 \cdot 69104} : 1 = 6 \cdot 7458 : 1.$$

The same result was obtained in a similar way by the synthesis of silver sulphide, Ag_2S, and its oxidation to silver sulphate Ag_2SO_4. Finally Stas analysed the chlorate, bromate, and iodate of silver, $AgClO_3$, $AgBrO_3$, and $AgIO_3$. The results of these analyses, and of the syntheses of AgCl, AgBr, and AgI, give the ratio:

$$Ag : O = 6 \cdot 7456 : 1,$$

which agrees closely with the former result. Compared with hydrogen, the atomic weight of silver is 107·66,

$$Ag : H = 6 \cdot 7456 \times 15 \cdot 96 : 1 = 107 \cdot 66 : 1.$$

Many other methods have been suggested for the indirect determination of the atomic weights of elements in terms of hydrogen. The preceding examples will suffice to illustrate the methods employed.

§ 31. **Selection from Different Determinations.**—Although no method of determination is free from error, the amount of error is very variable. Consequently the values for the atomic weights obtained by different methods do not coincide absolutely. But as Stas has proved by experiments, specially made for this purpose, that the atomic weights are constant and invariable values, under all known conditions, it follows that only one value can be accepted as correct. It is necessary to select this, the exact value, from the others. This problem is one frequently associated with difficulties, and requires much care and consideration.

The analytical or synthetical methods employed must be submitted to a critical examination for the purpose of ascertaining the extent and the sources of error.

The results of the method which is most free from error are naturally preferred. The magnitude of the error involved in a particular method can often, but not always, be ascertained by making several determinations by the method and comparing the results. This cannot, however, be done when all the determinations contain a common error, a so-called 'constant' error; *e.g.* if in a case of oxidation the reaction is not quite complete, a definite quantity of the element will always yield too little oxide, and in all such experiments the atomic weight will be found too high.

If the precipitation of an element is accompanied by a certain loss, the total weight of the element will not be obtained, and the atomic weight will be low in all the determinations.

The constant errors are more to be feared than the casual errors, because they lead us to believe in a degree of accuracy which in reality does not exist. This explains why Gauss's method of least squares is seldom used in atomic weight determinations, although, as a rule, it is well adapted for determining the extent of errors of experiment.

A complete analysis or synthesis offers a certain guarantee against constant or occasional errors. If the sum of the constituents is very nearly equal to the weight of the compound, this indicates that no considerable loss has taken place, or that the loss is exactly balanced by a gain of foreign matter taken up during the analysis. The loss of constituents exactly balancing the gain in foreign matter is a very rare occurrence. A partial decomposition may be mistaken for a complete one, and thus occasion serious errors. Berzelius attempted to determine the atomic weight of vanadium by reducing its highest oxide in hydrogen. Roscoe afterwards proved that only $\frac{3}{5}$ of the oxygen in the oxide is removed and that $\frac{2}{5}$ remains in the residue, which Berzelius regarded as the pure element. The true atomic weight of V is 51·1, but Berzelius calculated it to be 137—*i.e.*, according to our present knowledge, V_2O_2.

The best guarantee against error of all kinds is secured when the atomic weight of an element has been determined by several distinct methods, and the results are found to agree.

§ 32. **Accuracy of the Atomic Weights.**—An examination of the numerous atomic weight determinations shows that there is an extraordinary difference in their degree of accuracy. The ratio between a small number of the atomic weights has been determined to the $\frac{1}{100000}$ part of their value (*e.g.*

between iodine and silver), and for a somewhat larger number of elements to the $\frac{1}{10000}$ part. The error in the case of other elements amounts to $\frac{1}{1000}$ of their value, and in the case of a few it is not less than one per cent. The relation between the atomic weights of hydrogen and oxygen, which is taken as the standard by which all other atomic weights are measured, may contain an error of one or two thousandths of its value. This possible error affects all the other atomic weights which are referred to this standard. But this uncertainty does not vitiate the accuracy of the stœchiometric calculations, as they are independent of the standard chosen. If we express the other possible errors in terms of this unit, then the error is not greater than 0·1 H for one third of the elements, and does not exceed 0·5 H for a second third. In the case of the remaining elements the error will amount to from 0·5 to 1, and in some cases, which require re-determining, may amount to two or more units.

§ 33. **Prout's Hypothesis.**—It has already been pointed out in § 31 that our investigations indicate that the atoms of one and the same elements are alike in all respects, but that the atoms of two or more different elements are dissimilar. Up to the present day, it has never been possible to convert one element into another. At the same time, it is improbable that the elements which have been discovered, or are yet to be discovered, are really primal forms of matter. Their large number and other reasons induce us to believe that just as the elements are the basis of the composition of all the compounds derived from them, so they in turn may prove to be combinations of units of a higher order. This idea originated almost at the same time as the atomic theory, but, in spite of much experimental and theoretical effort, it has never advanced beyond the stages of conjecture.

In 1815 an English chemist, Prout, published (at first anonymously) a conjecture of this kind. He observed that the atomic weights of many of the elements appeared to be rational multiples of the atomic weight of hydrogen, and might be represented by whole numbers. Prout's hypothesis is tempting in its simplicity, and for a time was favourably received by chemists, excepting by those who had made exact and accurate atomic weight determinations. This hypothesis has never received experimental confirmation; on the contrary, many atomic weights may be nearly but not exactly represented by whole numbers, and in all the cases which have been accurately examined the deviations from the whole numbers have proved to be greater than the possible or probable experimental error. This hypothesis has attracted a considerable amount of attention, but is opposed to the best atomic weight determinations of Berzelius, Marignac, Stas, and others.

§ 34. **Döbereiner's Triads.**—Another relation between the atomic weights, discovered by Döbereiner in 1829, has yielded better results. This chemist noticed that in many cases one member of a group of three analogous elements possesses an atomic weight which is approximately the mean of the other two. In other cases, three elements bearing a close resemblance to each other in their properties have nearly the same atomic weights.

Examples of the first class

Lithium	Li = 7·01
Difference	15·99
Sodium	Na = 23·00
Difference	16·03
Potassium	K = 39·03
Sulphur	S = 31·98
Difference	46·89
Selenium	Se = 78·87
Difference	46·13
Tellurium	Te = 125
Calcium	Ca = 39·9
Difference	47·4
Strontium	Sr = 87·3
Difference	49·6
Barium	Ba = 136·9
Chlorine	Cl = 35·37
Difference	44·39
Bromine	Br = 79·76
Difference	46·78
Iodine	I = 126·54

Examples of the second class

Iron	Fe = 55·88
Cobalt	Co = 58·9
Nickel	Ni = 58·69
Ruthenium	Ru = 101·4
Rhodium	Rh = 102·7
Palladium	Pd = 106·3
Osmium	Os = 190·3
Iridium	Ir = 192·5
Platinum.	Pt = 194·3

Döbereiner believed that the basis of a systematic classification of the elements might be found in these relations, but it was long before this idea was successfully developed. The attempts which were made in this direction by Pettenkofer (1851), Dumas (1859), and others could scarcely be successful, as at this time the atomic weights had not been deduced from the analytical results in a uniformly systematic manner. When this had once been accomplished, it was found possible to arrange all the elements in groups of three, four, or five members, in which the same differences of, approximately, sixteen, forty-six, and eighty-eight units occur.

When the old values for the atomic weights are used, some groups exhibit differences double those observed for other groups. As the difference is approximately identical in different groups, it follows that if the atomic weight of the first member of group X is larger than that of the first member of another group Y, then the second and third members of group X will have higher atomic weights than the corresponding members of group Y. It seemed possible that the systematic classification of the elements which Döbereiner strove to accomplish might be realised by arranging these groups in the order of their atomic weights. This idea could not be carried into effect, as many atomic weights had been incorrectly determined. An attempt to classify the elements according to the order of their atomic weights was also unsuccessful. The classification of the elements in groups of three, four, five, or six members, and the arrangement of these groups in the order of the atomic weights of their members could only be satisfactorily achieved when the atomic weights of vanadium, tantalum, indium, the cerium metals and several other elements had been re-determined and corrected.

I

				Li 7·01	Be 9·1	Bo 10·9	C 11·97
Diff.				15·99	15·2	16·1	16·3
	N 14·01	O 15·96	F 19·06	Na 23·00	Mg 24·3	Al 27·0	Si 28·3
Diff.	16·95	16·02	16·31	16·03	15·6	17·0	19·7
	P 30·96	S 31·98	Cl 35·37	K 39·03	Ca 39·9	Sc 44·0	Ti 48
Diff.	43·9	46·89	44·39	46·2	47·4	44·9	42·4
	As 74·9	Se 78·87	Br 79·76	Rb 85·2	Sr 87·3	Y 88·9	Zr 90·4
Diff.	44·7	46·1	46·78	47·5	49·6	49·3	49·5
	Sb 119·6	Te 125·0	I 126·54	Cs 132·7	Ba 136·9	La 138·2	Ce 139·9
Diff.	89·3						92
	Bi 208·9						Th 231·9

II

	V 51·1	Cr 52·0	Mn 54·8	Fe 55·88	Ni 58·6	Co 58·9
Diff.	42·6	43·9		45·5	44·1	47·4
	Nb 93·7	Mo 95·9		Ru 101·4	Rh 102·7	Pd 106·3
Diff.	88·3	87·7		88·9	89·8	88·0
	Ta 182	W 183·6		Os 190·3	Ir 192·5	Pt 194·3
Diff.		55·4				
		U 239·0				

III

	Cu 63	Zn 65·1	Ga 69·9	Ge 72·3
Diff.	44·6	46·7	43·7	46·5
	Ag 107·66	Cd 111·8	In 113·6	Sn 118·8
Diff.	89·0	88	90·1	87·6
	Au 196·7	Hg 199·8	Tl 203·7	Pb 206·4

§ 35. **Arrangement of the Elements in the Order of their Atomic Weights.**—Most of the groups in the second table are related to one of the groups in the first table by analogies in the properties of their members, and especially by the isomorphism of their compounds. Vanadium, V, is associated with phosphorus, P, and arsenic, As, by isomorphism; in the same way chromium, Cr, and molybdenum, Mo, are related to sulphur, S, and selenium, Se; by the isomorphism of the permanganates with the perchlorates, manganese, Mn, is associated with chlorine, Cl. The first table does not contain any elements analogous to iron, nickel, cobalt, and the six platinum metals; but copper, Cu, and silver, Ag, are related to sodium, Na; and zinc, Zn, to magnesium, Mg, and calcium, Ca; indium, In, to aluminium, Al; and tin, Sn, is isomorphous with silicon, Si, and titanium, Ti. We are therefore not only justified in joining these two tables together, but in uniting them to form the following table. The perpendicular columns contain not only closely allied elements, but also others which only bear an analogy to them in certain respects, but differ from them widely in other points.

Atomic Weights of the Elements[1]

—	I	II	III	IV	V	VI	VII	—
	Li 7·01	**Be 9·08**	**B 10·9**	**C 11·97**	**N 14·01**	**O 15·96**	**F 19·06**	
Diff.	15·99	15·2	16·1	16·3	16·95	16·02	16·31	
	Na 23·0	**Mg 24·3**	**Al 27·04**	**Si 28·3**	**P 30·96**	**S 31·98**	**Cl 35·37**	
Diff.	16·08	15·16	16·93	19·7	20·0	20·02	19·4	**Fe 55·88**
	K 39·03	**Ca 39·91**	**Sc 43·97**	**Ti 48·0**	**V 51·1**	**Cr 52·0**	**Mn 54·8**	**Co 58·9**
Diff.	24·15	25·2	25·9	24·3	23·8	26·87	25·0	**Ni 58·6**
	Cu 63·18	**Zn 65·10**	**Ga 69·9**	**Ge 72·3**	**As 74·9**	**Se 78·87**	**Br 79·76**	
Diff.	22·0	22·2	19·0	22·1	18·8	17·0	18 ?	**Ru 101·4**
	Rb 85·2	**Sr 87·3**	**Y 88·9**	**Zr 90·4**	**Nb 93·7**	**Mo 95·9**	— 98 ?	**Rh 102·7**
Diff.	22·5	24·5	24·7	28·4	25·9	29·1	28 ?	**Pd106·35**
	Ag107·66	**Cd 111·8**	**In 113·6**	**Sn 118·8**	**Sb 119·6**	**Te 125·0**	**I 126·54**	
Diff.	25·0	25·1	24·6	21·1				
	Cs 132·7	**Ba 136·9**	**La 138·2**	**Ce 139·9**	—	—	—	
			34·4					**Os 190·3**
	—	—	**Yb 172·6**	—	**Ta 182**	**W 183·6**	—	**Ir 192·5**
			31·1		26·9			**Pt 194·3**
	Au 196·7	**Hg 199·8**	**Tl 203·7**	**Pb 206·4**	**Bi 208·9**	—	—	
				23·5				
				Th 231·9		**U 238·8**		

In the horizontal rows of this table the elements are arranged in the order of their atomic weights. If the right side of each row is connected with the left side of the following row a single continuous series of all the elements will be produced. In this arrangement the nature and properties of the members will be represented as periodic functions of the atomic weights, changing systematically as the atomic weight increases from member to member, and returning to the beginning after a certain number of members. The periodicity may be more clearly indicated by means of the table at the end of this book. The table should be pasted on a wooden or pasteboard cylinder of suitable dimensions, so that the right and left sides meet.

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[1] Helium and argon are omitted from this table. See Appendix.

The first two periods or series each embrace seven elements.

	1	2	3	4	5	6	7
I	Li	Be	B	C	N	O	Fl
II	Na	Mg	Al	Si	P	S	Cl

The corresponding members closely resemble each other—*e.g.* lithium and sodium, beryllium and magnesium.

This resemblance continues in the third and fourth periods, so far as the first members are concerned; the following members do not exhibit corresponding properties, and it is not until we reach the seventeenth member after potassium that another alkali metal, rubidium, recurs. The next alkali metal, caesium, is again the seventeenth element after rubidium. Both metals are preceded by elements which are closely related to the last members of the first and second periods. On closer consideration these large periods are found to split up into two smaller periods, in which some of the properties of the elements recur at a shorter interval. This is seen in the following table:

	1	2	3	4	5	6	7	8	9	10
III	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co
	Cu	Zn	Ga	Ge	As	Se	Br			
IV	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd
	Ag	Cd	In	Sn	Sb	Te	I			
V	Cs	Ba	La	Ce						

The elements in the same column all have certain properties in common, but only the alternate elements bear a close resemblance to one another. After cerium, Ce, there is a gap of about forty units. This will probably be filled by the rare earth metals, which have not yet been sufficiently well investigated. Then comes ytterbium (the atomic weight of this metal has not been accurately determined) and tantalum; they are followed by elements resembling the former members, in the same order as in the preceding periods, but leaving some gaps and spaces:

1	2	3	4	5	6	7	8	9	10
—	—	Yb	—	Ta	W	—	Os	Ir	Pt
Au	Hg	Tl	Pb	Bi	—				
—	—	—	Th	—	U				

The gaps in this and the preceding tables will probably be filled by elements which have not yet been discovered. Several of the gaps which existed when the periodic system of the elements was first promulgated have been filled up by the discovery of scandium, gallium, and germanium, and by the correction of the atomic weights of indium, yttrium, cerium, and lanthanum.

It appears from the table on page 56 that a dozen elements are yet to be discovered. The majority of these gaps will probably be filled by rare earth metals with atomic weights lying between 140 and 180.

This natural and systematic arrangement of the elements, first attempted by Döbereiner and brought to perfection by the labours of Newlands, Mendeléeff and Lothar Meyer, is analogous to the classification in organic chemistry of compounds in homologous and heterologous series.

§ 36. **Periodicity of the Physical Properties of the Elements.**—If we examine the long series of elements from member to member, we find a change in the properties, sometimes gradual and sometimes sudden, which recurs in the following periods in a similar way, so that almost every property of an element occurs again in one or more of the later members, so that the properties of each individual element are determined by its position in the series. This is not only true of the chemical and physical properties of the elements, but also of the compounds.

This recurrence of the physical properties is very striking in the case of density, which regularly increases and decreases in each period. The connection between density and atomic weight is best exhibited by taking the atomic volume instead of the density—*i.e.* the volume occupied by the atomic weight instead of the weight of the unit volume. The simplest expression for the atomic volume is obtained by dividing the atomic weight by the density.

These quotients represent the volume of the atoms in the solid state compared with the volume occupied by the unit weight of liquid water as unity. As the absolute weight of an atom of hydrogen is not known, the unit of atomic weights is not known, and this unit of volume must remain an unknown quantity. But these quotients may be compared by means of another standard—*e.g.* the atomic weight of an element, expressed in grams, occupies in the solid state the same number of cubic centimetres as the value of the atomic volume. For example, the atomic volume of silver is 10·2, and therefore 107·66 grams of silver occupy 10·2 c.c.

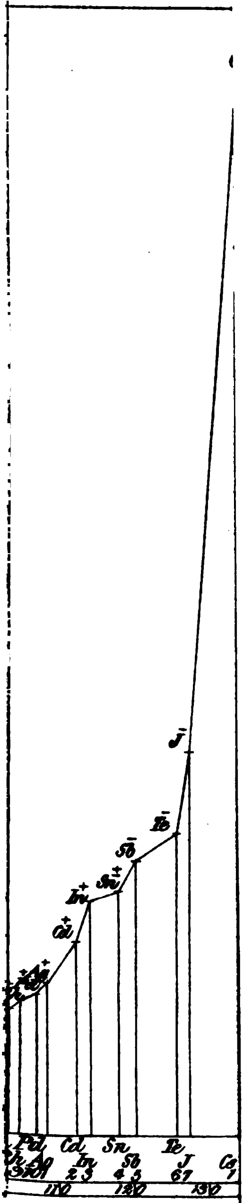
In the table on p. 60 the density D and the atomic volume V are given under the symbol of each element. The density begins at a minimum with the alkali metals, lithium, sodium, rubidium, caesium, and ascends from this in the first two periods to carbon and silicon ; in the following periods the density continues to increase after passing the homologues of these elements till it reaches the metals copper, ruthenium, osmium, and then sinks. In the atomic volumes the position is reversed – the maximum is at the alkali metals, and the minimum occurs at carbon, aluminium, nickel, ruthenium, osmium.

The relation between the atomic volume and atomic weight is more clearly depicted by the accompanying graphic representation. In this table the elements are arranged on the horizontal axis of the abscissæ at distances from zero proportional to their atomic weights. The position of each element is denoted by the corresponding symbol, and from each of these points an ordinate is drawn, which is proportional in length to the atomic volume of the element. By connecting the summits of all the ordinates by lines, we obtain a curve which clearly illustrates the relation of the atomic volume to the atomic weight. The alkali metals occupy a striking position at the five maxima. Those portions of the curve between the maxima resemble chains, which are broken at certain points, because the elements which should occupy these positions are either unknown or have not yet been sufficiently investigated. The great regularity in the course of the curve indicates that the curve will, without doubt, closely follow the dotted course. On this account the probable values, in round numbers, of the density and atomic volumes of these elements have been inserted in the preceding table. In order to distinguish the real from the hypothetical values, notes of interrogation are affixed to the latter.

Density and Atomic Volumes of the Elements.

—	I	II	III	IV	V	VI	VII	VIII		
	Li	Be	B	C	N	O	F			
D	*0·59*	*1·85*	*2·68*	*3·3*	*3* (?)	*2* (?)	*1·5* (?)			
V	11·9	4·9	4·0	3·6	5 (?)	8 (?)	13 (?)			
	Na	Mg	Al	Si	P	S	Cl			
D	*0·97*	*1·74*	*2·56*	*2·49*	*2·3*	*2·04*	*1·38*			
V	23·7	13·9	10·6	11·4	13·5	15·7	25·6			
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
D	*0·86*	*1·57*	*2·6* (?)	*3·7* (?)	*5·5*	*6·8*	*8·0*	*7·8*	*8·5*	*8·8*
V	45·4	25·4	17 (?)	13 (?)	9·3	7·7	6·9	7·2	6·9	6·7
	Cu	Zn	Ga	Ge	As	Se	Br			
D	*8·9*	*7·15*	*5·96*	*5·47*	*5·67*	*4·6*	*2·97*			
V	7·1	9·1	11·7	13·2	13·2	17·1	26·9			
	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd
D	*1·52*	*2·50*	*3·6* (?)	*4·15*	*7·06*	*8·6*	—	*12·26*	*12·1*	*11·5*
V	56·1	34·9	25 (?)	21·7	13·0	11·1	—	8·3	8·5	9·2
	Ag	Cd	In	Sn	Sb	Te	I			
D	*10·5*	*8·65*	*7·42*	*7·29*	*6·7*	*6·25*	*4·94*			
V	10·2	12·9	15·3	16·3	17·9	20·2	25·6			
	Cs	Ba	La	Ce						
D	*1·88*	*3·75*	*6·2*	*6·7*						
V	70·6	36·5	22·5	21·0						
					Ta	W	—	Os	Ir	Pt
D					*10·8*	*19·13*	—	*22·48*	*22·42*	*21·50*
V					16·9	9·6	—	8·5	8·6	9·1
	Ag	Hg	Tl	Pb	Bi					
D	*19·3*	*14·2*	*11·86*	*11·38*	*9·82*					
V	10·1	14·1	17·2	18·1	21·3					
				Th	—	U				
D				*11·2*	—	*18·69*				
V				20·9	—	12·6				

It is very remarkable that the properties of all the elements appear to be determined by their position on this curve. The descending portions of the curve from the maximum to the minimum, and a little beyond, are entirely occupied by less easily fusible and non-volatile elements, and, as a rule, the lower the element is on the curve the more infusible it is found to be. Only easily fusible, and as a rule volatile elements occur on the ascending portions of the curve.



Longmans, Green & Co, Lon

In the first period, nitrogen, oxygen, and fluorine are gases, in the second period chlorine; but phosphorus and sulphur are easily fusible and volatile. In the next period the series of volatile elements begins with zinc (or perhaps even with copper). In the following period, the volatile elements begin with silver, which can be distilled by means of the oxyhydrogen blowpipe, and in the last incomplete period mercury is the first volatile element. This relation may be expressed in general terms by saying that when the atomic volume decreases with an increasing atomic weight the elements are refractory and non-volatile; but when the atomic volume increases as the atomic weight increases the elements are easily fusible and volatile.

Other properties change twice in these larger periods. This is the case with the metallic nature of the elements as exhibited by their malleability. The elements at the maximum of the curve and their immediate successors are metals. They are followed by brittle elements down to the minimum. These are succeeded by malleable metals, which are separated from the metals at the maximum by brittle non-metals and semi-metals—*e.g.*

K, Ca, (Sc ?), malleable;
Ti, V, Cr, Mn, brittle;
Fe, Co, Ni, Cu, Zn, Ga, malleable;
Ge, As, Se, Br, brittle or non-metallic.

The malleability is the same in the following periods. Other physical properties change in a similar way, but some of these properties have not yet been sufficiently investigated. The elements on ascending portions of the curve are without exception diamagnetic, those on the falling part of the curve are magnetic. The optical properties, crystalline form, and expansion by heat exhibit similar regularities.

§ 37. **Periodicity of the Electro-chemical Properties.**—The intimate connection between the chemical properties and the atomic weight proceeds from the fact that the whole system of arrangement consists in bringing together the natural families of elements which have been developed from Döbereiner's triads.

The chemical elements and their compounds exhibit certain contrasts in their nature. These are indicated by the terms 'positive' and 'negative.' The use of these terms arises from the close relation between chemical and electrical properties. As a rule, when two or more bodies of different composition are brought in contact with each other, both are electrified —one becoming positive, the other negative. The greater the difference between the composition of the two substances the greater the electrical excitement will be. The difference which exists between the two bodies is called the electro-chemical difference. The direct measurement of the electric charge produced by the contact of heterogeneous bodies is difficult. But the electro-chemical nature of the substances can be determined by another method. Many liquids and some solids are decomposed by the electric current. In this act of electrolysis, those constituents which are positive on contact are liberated with the positive electricity and those which become negative with the negative electricity, so that the electro-chemical nature of the constituents is easily recognised. The difference in the electro-chemical nature of a substance is not absolute, but merely relative, so that one element can be positive with regard to a second element and negative to a third. It has also been observed that a positive element in a compound can generally be replaced by a more positive and a negative by a more negative. This replacement of one element by another affords another means of ascertaining the electro-chemical nature of an element. The oxides and hydroxides of the positive elements have basic properties (*i.e.* they neutralise acids); the oxides, hydroxides, and some of the hydrides of the negative elements are acids.

If the elements are divided into the two classes—electro-negative and electro-positive—these properties are regularly divided in the periods. In the atomic volume table, the positive elements are denoted by + and the negative by —. The positive nature changes in the same way as the metallic nature and malleability, *i.e.* twice in the large periods of atomic volumes.

The first family in the table on page 56 consists of positive elements, the alkali metals, Li, Na, K, Rb, Cs; the positive character increases with the atomic weight, and caesium is not only the most electro-positive metal of this group but of all the elements. The metals Be, Mg, Ca, Sr, Ba, in the second family, closely resemble these metals in their electro-positive nature; again, we find the metal with the highest atomic weight, barium, is the most electro-positive. In the third family, containing Bo, Al, Sc, Y, La, Yb, the electro-positive nature is much feebler. The hydroxide of boron is a feeble acid, and aluminium hydroxide exhibits the properties of a weak acid as well as of a strong base: here again the negative character grows feebler and the positive stronger, as the atomic weight increases. In the fourth family C, Si, and Ti yield acids, but the higher members Zr, Ce, and Th have a more positive character. The elements in all these four families have one property in common: they form very stable compounds with oxygen, and consequently their oxides are difficult to reduce.

The four sub-groups, which are entirely composed of heavy metals, are of an opposite character:

I	II	III	IV
Cu	Zn	Ga	Ge
Ag	Cd	In	Sn
Au	Hg	Tl	Pb

These elements are easily obtained from their oxides and analogous compounds by reduction. In the first two groups, the facility with which the compounds are reduced increases with the atomic weight. In the first and second family the positive character decreases as the atomic weight increases. This is exactly opposite to the behaviour of the refractory light metals of this family. Nothing is known of the third group in this respect, but in the fourth group lead (Pb) is more positive than tin (Sn); the positive character, as usual, increasing with the atomic weight.

The same contrasts occur in the following three families, only with this difference, that the first members do not belong to the refractory, but to the easily reducible, elements, with the exception of phosphorus, which is not so easily reducible as arsenic, antimony, and bismuth, but more easily than vanadium, niobium, and tantalum. The chief group is here formed of the easily reducible elements :

V.	N	P	As	Sb	Bi
VI.	O	S	Se	Te	—
VII.	Fl	Cl	Br	I	—

The sub-group is composed of the refractory elements :

V.	V	Nb	Ta	—
VI.	Cr	Mo	W	U
VII.	Mn	—	—	—

The three groups generally embraced in family VIII. are easily reducible :

Fe	Ru	Os
Co	Rh	Ir
Ni	Pd	Pt

A comparison of the chemical properties with the position on the curve of atomic volumes shows that the refractory elements occur on the descending, and the easily reducible elements on the ascending, portions of the curve, but the change from positive to negative is seen on both portions of the curve.

§ 38. **Theoretical Prediction of Properties.**—The close connection between atomic weights and properties renders it possible to predict the unknown properties of an element as soon as its atomic weight is ascertained, and, on the other hand, the atomic weight can be deduced approximately from the chief properties of an element.

When the ‘Periodic Law’ was first propounded, scandium, gallium, and germanium were unknown, and the positions these elements now occupy were represented by blank spaces. Mendeléeff ventured to predict the properties of these undiscovered elements, and his predictions were afterwards verified when the elements were discovered and investigated. The speedy recognition of the value of this systematic arrangement of the elements was, to a great extent, the result of this happy verification of Mendeléeff's predictions. On the other hand, some atomic weights had been incorrectly determined, and attention was called to this fact by the circumstance that these elements did not fit into the system.

The atomic weight of caesium was ten units too low; indium was only two-thirds of the value now in use. Earlier determinations placed platinum before iridium and iridium before osmium, but the properties of these metals indicated that the order should be reversed, and this has been confirmed by the new atomic weight determinations of K. Seubert. The question whether the atom of beryllium corresponds to two or three equivalents—that is, whether the atomic weight is $2 \times 4{\cdot}54 = 9{\cdot}08$ or $3 \times 4{\cdot}54 = 13{\cdot}62$—has been decided by the followers of the periodic system in favour of the first assumption, because there is no space for an element with the atomic weight, 13·6, between carbon ($C = 11{\cdot}97$) and nitrogen ($N = 14{\cdot}01$), and an element possessing the properties of beryllium would be out of place in such a position. The question was definitely settled by the determination of the vapour density of beryllium chloride by Nilson and Pettersson. This result has also materially influenced the recognition of the Periodic System.

§ 39. **Periodicity of Valency.**—The elements differ widely in their combining power. The atoms of some elements can only combine with a single atom, but the atoms of other elements can each unite with two, three, four, or more other atoms. They have double, treble, &c., the power of the other atom, and are said to be di-, tri-, tetra-, penta- or hexavalent, or they are said to have two, three, or more affinities. Hydrogen also forms the standard of comparison, as it does in the case of the equivalent and atomic weights. The combining powers of the chemical elements vary regularly with the atomic weights.

All those elements are called 'monovalent' that have an atomic weight equivalent to one atom of hydrogen; if their atoms unite with or displace two atoms of hydrogen, they are said to be divalent.

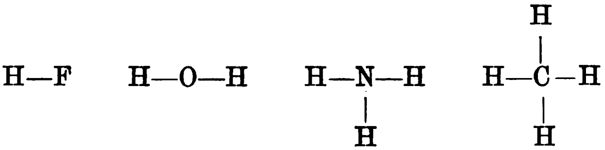
The determination of this property of chemical valency is simple enough in principle. For, if the atomic weight of an element is equal to its equivalent weight (§ 11), the element is monovalent; if the atomic weight is double the equivalent weight, it contains two equivalents and the element is divalent.

Generally speaking, the chemical valency is determined by the number of equivalent weights contained in the atomic weight. The chemical valency determined by this method is a periodic function of the atomic weight. Before studying this relationship, it is necessary to consider the methods of determining valency.

§ 40. **Determination of Chemical Valency.**—The valency of an element is most easily determined from the composition of the molecule of its hydrogen compounds. These hydrides are not numerous; they may be divided into four types:

I	II	III	IV
HF	H_2O	H_3N	H_4C
HCl	H_2S	H_3P	H_4Si
HBr	H_2Se	H_3As	—
HI	H_2Te	H_3Sb	—

As the hydrogen atom can only unite with a single atom of its own class to form the molecule H_2, we must assume that the hydrogen atoms contained in the compounds under II., III., and IV. are united to the other constituents. These compounds may be represented graphically by the formulæ:



$$\mathrm{H{-}F} \qquad \mathrm{H{-}O{-}H} \qquad \begin{array}{c} \mathrm{H{-}N{-}H} \\ | \\ \mathrm{H} \end{array} \qquad \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}$$

The dashes indicate the manner in which the atoms are supposed to be united together. As the elements in the four types are incapable of combining with a larger number of hydrogen atoms, we regard, so far as their compounds with hydrogen are concerned, fluorine, chlorine, bromine, and iodine as monovalent; oxygen, sulphur, selenium, and tellurium as divalent; nitrogen, phosphorus, arsenic, antimony as trivalent; carbon, silicon as tetravalent.

As F, Cl, Br, and I are monovalent in the compounds in the first group and have the same valency as hydrogen, they may be used like hydrogen, for the purpose of determining the valency of other elements. This is all the more satisfactory, as their compounds are much more numerous than those of hydrogen. A comparison of the fluorides, chlorides, bromides and iodides of the first four families shows that their compounds correspond to the four types which have just been mentioned, *e.g.*:

I	II	III	IV
$LiCl$	$BeCl_2$	BCl_3	CCl_4
$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$
KCl	$CaCl_2$	$ScCl_3$	$TiCl_4$
$CuCl$	$ZnCl_2$	$GaCl_3$	$GeCl_4$
$RbCl$	$SrCl_2$	YCl_3	$ZrCl_4$
$AgCl$	$CdCl_2$	$InCl_3$	$SnCl_4$
$CsCl$	$BaCl_2$	$LaCl_3$	($CeCl_4$?)
$AuCl$	$HgCl_2$	$TlCl_3$	$PbCl_4$

The chemical valency is constant for each family, and with an increasing atomic weight, rises from one family to the next by one unit.

The following families behave in a similar way, but at first sight the relationship appears somewhat more complicated, the composition of the typical hydrides indicating that the valency decreases, thus:

V	VI	VII
NH_3	OH_2	FH
PH_3	SH_2	ClH

Certain chlorine compounds of these elements have an analogous composition:

V	VI	VII
NCl_3	OCl_2	$ClCl$
PCl_3	SCl_2	ICl

But these and similar compounds do not contain the maximum amount of chlorine or other monovalent atoms, with which the elements are capable of uniting. Compounds of the following composition are known:

V	VI	VII
NH_4Cl	SCl_4	ICl_3
PCl_5	$SeCl_4$	—
VCl_4	$TeCl_4$	–
$NbCl_5$	$CrCl_3$	–
$SbCl_5$	$MoCl_6$	—
$TaCl_5$	WCl_6	—

Some of these compounds are very unstable: ammonium chloride, phosphorus pentachloride, and iodine trichloride decompose on volatilisation, *e.g.*: $NH_4Cl=NH_3+HCl$; $PCl_5=PCl_3+Cl_2$; $ICl_3=ICl+Cl_2$; others can be converted into vapour without decomposition, *e.g.*: $NbCl_5$, $TaCl_5$, $TeCl_4$, $MoCl_5$, WCl_6. This difference in the behaviour of the compounds is explained by the fact that the affinity of the negative elements for chlorine and its analogues is feeble, and consequently the chlorine atoms are easily separated from the compound. The behaviour of sulphur is very remarkable: the tetrachloride SCl_4 can only exist at —20° C.; even at 0° C. it begins to decompose into SCl_2, and on distillation half the residual chlorine is lost. Sulphur does not form any definite compounds with bromine and iodine. Phosphorus combines with five atoms of fluorine to form a stable compound. PCl_5 and PBr_5 easily part with two atoms of chlorine or bromine respectively: but phosphorus can only unite with three atoms of iodine; as a rule it only combines with two, forming PI_2.

We may assume that the difference in the behaviour of the elements belonging to families V. and VI. towards the non-metals is not due to a difference in their valency, but is probably caused by a difference in the force with which they attract the monovalent elements.

This assumption is confirmed by an examination of the oxygen compounds. As an atom of oxygen is equivalent to two atoms of hydrogen and is divalent, any other atom which has the power of uniting with one atom of oxygen is also divalent. One trivalent atom could combine with oxygen in the proportion of one to one and a half, or, more correctly, two trivalent atoms can unite with three atoms of oxygen. The radical hydroxyl —OH is formed by the union of one atom of hydrogen with one atom of oxygen; as the oxygen still has the power of uniting with a second atom, the radical is monovalent. The valency of an element is represented by the number of hydroxyls with which an atom combines, or by twice the number of oxygen atoms which in its oxide would be united with one atom. In order to permit of a uniform comparison, the formulæ of the oxides in the following table are given as though they contained two atoms of the other element, even where the molecule may only contain one atom.

Oxides

I Monovalent	II Divalent	III Trivalent	IV Tetravalent	V Pentavalent	VI Hexavalent	VII Heptavalent	VIII Octovalent
Li_2O	Be_2O_2	B_2O_3	C_2O_4	N_2O_5	—	—	—
Na_2O	Mg_2O_2	Al_2O_3	Si_2O_4	P_2O_5	S_2O_6	Cl_2O_7	—
K_2O	Ca_2O_2	Sc_2O_3	Ti_2O_4	V_2O_5	Cr_2O_6	Mn_2O_7	—
Cu_2O	Zn_2O_2	Ga_2O_3	Ge_2O_4	As_2O_5	Se_2O_6	Br_2O_7	—
Rb_2O	Sr_2O_2	Y_2O_3	Zr_2O_4	Nb_2O_5	Mo_2O_6	—	Ru_2O_8
Ag_2O	Cd_2O_2	In_2O_3	Sn_2O_4	Sb_2O_5	Te_2O_6	I_2O_7	—
Cs_2O	Ba_2O_2	La_2O_3	Ce_2O_4	Ta_2O_5	W_2O_6	—	Os_2O_8
Au_2O	Hg_2O_2	Tl_2O_3	Pb_2O_4	Bi_2O_5	U_2O_6	—	—

This table shows the remarkable relation which exists between valency and atomic weight. The number of each family indicates its valency. In families I. to VII. only oxygen and fluorine are missing; no oxide of the latter element has as yet been prepared. In VIII. iron is omitted; the highest oxide, the anhydride of ferric acid, is unstable and has not been satisfactorily investigated. The same is true of the highest oxides of Co, Ni, Rh, Pd, Ir, Pt.

A few examples of the hydroxides will suffice:

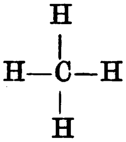
	Hydroxides		Valency	Hydrides
I.	NaOH	$=Na(OH)$	$1 \times 1 = 1$	—
II.	MgO_2H_2	$=Mg(OH)_2$	$2 \times 1 = 2$	—
III.	AlO_3H_3	$=Al(OH)_3$	$3 \times 1 = 3$	—
IV.	SiO_4H_4	$=Si(OH)_4$	$4 \times 1 = 4$	SiH_4
V.	PO_4H_3	$=PO(OH)_3$	$3 \times 1 = 3$	PH_3
VI.	SO_4H_2	$=SO_2(OH)_2$	$2 \times 1 = 2$	SH_2
VII.	ClO_4H	$=ClO_3(OH)$	$1 \times 1 = 1$	ClH

Here again the valency is indicated by the number of the family, showing the close relation between valency and atomic weight.

It is to be noted that families V., VI., VII. do not exhibit the same valency towards hydrogen and the metals that they do towards oxygen. Beginning with family IV., the valency increases one unit for oxygen and other negative elements, but decreases one unit for hydrogen and the positive elements, as is shown in the preceding tables.

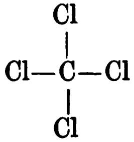
§ 41. **Possible Errors in the Determination of Chemical Valency.**—There are many other compounds, besides those mentioned in the preceding section, which can be used for determining the chemical valency of an element. Most of these yield a smaller value, but some give a larger value for the valency.

The valency is always too low when the element in question is not combined with the maximum number of atoms; that is to say, when some of its affinities remain unsaturated. The tetravalent carbon atom can unite with four monad atoms, such as hydrogen or chlorine, or two divalent oxygen atoms:



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Marsh Gas



$$\begin{array}{c} Cl \\ | \\ Cl-C-Cl \\ | \\ Cl \end{array}$$

Carbon Tetrachloride

$$O=C=O$$

Carbon Dioxide

When a limited supply of oxygen is passed over an excess of red-hot charcoal, then the carbon atoms cannot take up the maximum amount of oxygen, but form carbon monoxide.

The molecule of this compound is represented by the formula

$${}^{*}_{*}{=}C{=}O.$$

It would be incorrect to conclude from the composition of this compound that carbon is divalent; for two unsaturated affinities are also present, as indicated by the asterisks. This is shown by the fact that the compound unites with two atoms of chlorine, forming phosgene gas, or carbonyl dichloride.

$${}^{Cl}_{Cl}{=}C{=}O.$$

The valency of nitrogen cannot be deduced from the composition of nitric oxide (NO), nitrogen peroxide (NO_2), nitrosylchloride (NOCl), and similar compounds: they are known as unsaturated compounds, or as compounds containing unsaturated affinities. Those metals which only contain one atom in the molecule (§ 27), *e.g.* mercury, cadmium, and zinc, belong to this class.

There is another class of compounds which cannot be regarded as unsaturated, although the number of monovalent atoms does not correspond to the valency of the polyvalent atoms, viz. all those compounds containing more than one polyvalent atom in the molecule. In such compounds a certain number of valencies are used up in the union of the polyvalent atoms with one another, how many are in this way employed it would be difficult to decide.

It would be very difficult to ascertain the correct valency of carbon if we were only acquainted with the following compounds: ethane C_2H_6, ethylene C_2H_4, and acetylene C_2H_2.

A correct determination of the valency may be attempted by taking into account the affinities required for the purpose of linking together the polyvalent atoms: but this process may lead to erroneous conclusions. If we apply it to ethane we obtain the correct result: 6 affinities for H and 2 for C; total 8. But in the case of ethylene we only obtain 2 for C and 4 for H, total 6; and for acetylene 2 for H and 2 for C, total 4. According to these last results carbon might erroneously be considered as only di- or tri-valent.

But the composition of marsh gas shows that carbon is tetravalent, and the fact that the carbon is combined with less hydrogen in ethylene and acetylene than it is in ethane, is accounted for by the hypothesis that the carbon atoms are attached to each other by more than one affinity, thus:

$$\begin{array}{ccc} H_3\equiv C-C\equiv H_3 & H_2=C=C=H_2 & H-C\equiv C-H \\ \text{Ethane} & \text{Ethylene} & \text{Acetylene} \end{array}$$

It follows from these considerations that the chemical valency can only be deduced with certainty from the composition of those compounds which only contain one atom of the polyvalent element in the molecule. If more than one polyvalent atom is present, we do not know how many affinities are used in uniting the several polyvalent atoms together. We must also carefully satisfy ourselves of the absence of unsaturated affinities in the compound.

It is often difficult to decide whether this is the case, as the compound may not contain the full number of monovalent atoms if the element has feeble affinities.

The determination of the valency is a problem requiring great care in its solution, and it is not surprising that in the case of many elements the valency has not always been correctly determined, and that in many instances too low a value has been assigned.

§ 42. **Irregularities of the Chemical Valency.**—There are exceptions to the marked regularity in the relation of chemical valency to atomic weight. Certain compounds undoubtedly contain more chlorine, bromine, or oxygen than corresponds to their chemical valency. Many of these compounds may be regarded as molecular aggregations, formed by several complete molecules crystallising together. The beautiful crystalline compound PCl_3Br_4 may be regarded as $PCl_3Br_2 + Br_2$, or as $PCl_3 + Br_2 + Br_2$; in the same way the unstable tri-iodide of potassium may be considered to be $KI + I_2 = KI_3$. But all such compounds cannot be regarded in this light. Auric chloride, $AuCl_3$, is undoubtedly a true chemical compound; and gold must be trivalent, not monovalent, as we should expect from its being a member of the first family. The molecular weight of cupric oxide, CuO, is not known, as the oxide is non-volatile. Its formula may be Cu—O—O – Cu; but cupric chloride, $CuCl_2$, could not have an analogous formula. Copper is isomorphous with divalent zinc, and must therefore be divalent. It is shown to be a member of the first family by the fact that the chloride, $CuCl_2$, is not volatile, but is decomposed by heat, losing half its chlorine, yielding cuprous chloride. The molecular weight deduced from the vapour density determination of Victor Meyer corresponds to Cu_2Cl_2, Cl—Cu—Cu—Cl, in which copper is again divalent. At present we can only point out these exceptions without attempting to offer any explanation.

§ 43. **Theoretical Significance of Chemical Valency. Nature of Affinity.**—As science is not satisfied with a simple knowledge of facts, but endeavours to investigate their causal connection, theoretical chemistry has attempted to solve the problem of explaining the remarkable fact, that the chemical valency of different elements undergoes a systematic variation. It is very difficult to find an explanation, as very little is known as to the cause of the formation of chemical compounds. The cause is termed affinity, because the old chemists held that only those bodies are capable of uniting which possess a certain likeness or affinity for each other. Exactly the opposite view now prevails: namely, that the more unlike two bodies are, the more readily will they combine together; but the term affinity still survives.

Affinity is generally considered to be an attractive force existing in the atoms. This hypothesis is not the only one possible, nor is it, indeed, the most probable, but it is the most convenient, and consequently the most generally accepted. This hypothesis will be used for the present, and the consideration of other hypotheses (still imperfectly developed) which do not require the assumption of an attractive force, will be postponed. Affinity is probably closely allied to, if not identical with, electrical attraction; but no definite statement on this point can be made at present.

Affinity only acts at short distances; for bodies combine or decompose one another only when in direct contact. It is not in any way directly identical with the attraction which is produced by the ordinary electric charge or by magnetisation, which work at relatively large distances. We may imagine such a division of the magnetic or electric masses in the atom, as to produce an attractive force which could only be effective at a very small distance. But at present the state of our knowledge is not ripe for speculations of this nature.

Leaving aside the question of the true nature of affinity, we may still be able to draw some conclusions from the differences of chemical valency.

There is no doubt that the effect of affinity is to keep the atoms in a compound at a definite distance from one another, for the space which a compound occupies in the solid or fluid state is fixed and definite. It varies regularly with the temperature and pressure, but depends on the nature of the constituents. The atoms cannot be immovable in the positions which the affinities have caused them to assume; for, according to the mechanical theory of heat, not only the molecules as such, but also the atoms in the molecules, are in a state of active motion, oscillating or rotating round points of equilibrium.

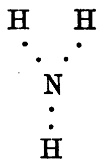
In the solid state the molecules of most bodies arrange themselves systematically, forming crystals. The form of the crystal is determined by the composition of the molecules and the nature of the atoms contained in the molecule, and is characteristic of both. As the different parts of a crystal exhibit certain points of difference, and the nature of this difference depends on the composition of the molecules and the nature of the atoms, it seems probable that these points of difference must already exist in the atoms and molecules themselves. The attractive force of affinity is active at these points. It endeavours to attract the other atoms and keep them in positions, which lie in these lines of force at a definite distance from the centre of gravity of the first atom. The distances between the centres of gravity may vary considerably for different atoms. There will be only one such position in the vicinity of a monovalent atom, in which a second atom can be fixed; but there will be two such points for a divalent and three for a trivalent atom, &c.

We may also venture to determine the position of these points in space. In the case of a compound consisting of two monovalent atoms only the distance between the atoms is fixed; the system will be in a state of equilibrium in any position. This may be the reason why compounds formed of two monovalent atoms generally crystallise in the regular system. A polyvalent atom requires a number of points corresponding to its chemical valency; these positions must be symmetrically arranged, at equal distances from the centre of gravity of the polyvalent atom. If this is not the case an exchange in the position of the atoms will produce 'isomeric' compounds—that is, compounds possessing the same composition, but exhibiting dissimilar properties. For example, there would be two potassium hydroxides, $K - O - - - H$, and $H - O - - - K$, and two amides of potassium, $\begin{matrix} H - \\ H - \end{matrix} N - - - K$, and $\begin{matrix} H - \\ K - \end{matrix} N - - - H$. Instances of what appeared to be examples of this kind of isomerism have from time to time been discovered, but on closer investigation they have invariably been proved to be spurious. It is, therefore, exceedingly probable that the points are symmetrically arranged at equal distances round the surface of a sphere. In a divalent atom the points will be diametrically opposite each other; in a trivalent atom the points will be arranged in a circle, at angles of 120°; in a tetravalent atom the points will be arranged in space like the angles of a regular tetrahedron; in a hexavalent atom the points will occupy the solid angles of an octahedron, or the centres of the faces of a cube; in an octovalent atom the points are arranged like the corners of a regular cube, or the centres of the faces of an octahedron. A perfectly symmetrical arrangement of five or seven points on the surface of a sphere is not possible, but it is probable that in this case the arrangement will be as symmetrical as possible.

Starting from these assumptions, it is easy to represent the configuration of the molecules, which are composed of monovalent atoms and only one polyvalent atom. A compound consisting of two monovalent atoms, or two monovalent and one polyvalent atom, is represented by a formula lying in a straight line :—

$$H - - Cl \qquad\qquad H - - O - - H$$

One trivalent and three monovalent atoms lie in a plane :—



$$\begin{matrix} H & & & & H \\ \cdot & & & & \cdot \\ & \cdot & & \cdot & \\ & & N & & \\ & & \cdot & & \\ & & \cdot & & \\ & & H & & \end{matrix}$$

One tetravalent and four monovalent atoms are arranged round the centre of a tetrahedron, at the solid angles. In fact, physical investigations of such compounds have made it exceedingly probable that their molecules really possess this form.[1]

It is difficult to follow this hypothesis when the monovalent atoms are wholly or partly replaced by polyvalent atoms, for one atom cannot occupy several positions at the same time. Attempts to overcome this difficulty are made by assuming that the atom alternately occupies the different positions, moving between them like a pendulum, or rotating about them. This view receives support from the observation that compounds containing polyvalent atoms attached to each other by multiple linkings occupy a larger space than those compounds do in which the polyvalent atoms are united together by a single linking. Again, it is observed that those carbon compounds which contain doubly or trebly linked carbon atoms easily split up at the points where the double or treble linking exists. Great importance must not be attached to such speculations at present, as they are much too hypothetical; but they may serve a useful purpose by enabling us to survey a variety of observations from a common standpoint.

§ 44. **Investigation of the Constitution of Chemical Compounds.**—The chemical valency of the elements and the composition of their compounds are intimately related. Not only the number of the atoms, but their arrangement in the molecule, depends on the valency of the elements. The possibility of investigating and ascertaining the manner in which the atoms are arranged was for a long time a disputed question. Although some chemists attempted to investigate the arrangement of the atoms, others looked upon such investigations as absolutely valueless. But even the followers of the latter school could not avoid holding certain views regarding the manner in which the atoms combine together to form compounds, for they rejected as unwarranted the doubts which existed as to the correctness and permissibility of their views. This dispute lasted more than twenty years, and, strange to say, it ended in the overthrow of these old dogmas by new hypotheses, by means of which we have acquired an unexpected insight into the nature of chemical compounds. At the present day the investigation of the 'constitution' or 'structure' of chemical compounds is one of the chief problems of the science; more particularly is this the case in organic chemistry, which treats of the compounds of carbon. In the course of the last fifty years these investigations have been brought to such a state of perfection, that it is now usual to dogmatically insert the results of such investigations in text-books as the fixed truth, without giving any exact account of the methods by which such intimate knowledge has been achieved.

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[1] Conclusions drawn from the friction of gases, with reference to the size of the section of molecules, appear to confirm these views.

It is desirable to know the exact grounds on which our knowledge rests, not only in the interests of those who specially devote themselves to such subjects, but also in the interests of the general history of civilisation and the history of science in particular. These investigations form one of the most striking examples of the power of the mind to penetrate into things which are as a sealed book to our senses alone. The path which the science of chemistry pursued to attain its present position was long, and not entirely free from error. But in looking back we can separate the essential from the non-essential and gain without difficulty a clear idea of the chief features of this development.

The chief difference between our present views and the older conceptions consists in this: formerly it was more or less explicitly assumed that a chemical compound was held together by the total attractive force of the affinities of all the atoms contained in it, but as our knowledge increased it was gradually recognised that, although the total attractive force is not without influence, the real chemical union is between atom and atom and that the atoms are attached to each other like the links in a chain, the continuity ceasing if even a single link of the chain is removed. This kind of combination is termed 'atomic linking'; the idea involved was not a sudden growth, but was the gradual outcome of previous conceptions.

The necessity of studying the atoms themselves was clearly stated by A. Kekulé in 1857, and by A. S. Couper in 1858. The doctrine of atomic linking is the outcome of the investigation of organic compounds, and at the present day it is chiefly applied to organic bodies ; but many conclusions as to the constitution of inorganic compounds have been deduced by its aid.

The theory of atomic linking first gave a satisfactory explanation of the observation that two or more chemical compounds having the same composition may exhibit widely different properties. This remarkable phenomenon has long been known as 'isomerism,' from *ἴσος*, same, and *μέρος*, the part. Isomeric bodies are those which contain the same constituents, *ἴσα μέρη*. We distinguish between 'metamerism' and 'polymerism'; metamerism embraces those cases in which the constituents are present in exactly the same number and quantity, but are differently arranged: the grouping of the constituents has been altered by a change of position, 'metastasis.' 'Polymerism,' or, better, 'pleomerism,' applies to those compounds in which the relative proportion between the constituents is the same, but the absolute number of atoms contained in the molecular weight of one compound is double or treble the number contained in the other.

There are several methods of investigating atomic linking which mutually support and supplement one another. In many simple cases the atomic linking can be deduced on purely theoretical grounds from the composition and molecular weight of the compound and the chemical valency of its constituents. But this can be done only when a single form of combination is possible, and the composition only permits of one interpretation. When the conditions are not so simple we make use of analysis and synthesis, assuming that those constituents which remain combined together when a compound is decomposed were previously united, and inversely in building up a compound, the parts which were united before remain united after the combination has taken place. This assumption is not always correct. Finally, we have a very important aid to such investigations, in the connection which has been established by innumerable comparisons between the chemical and physical properties of a body and its atomic linking.

§ 45. **Theoretical Determination of the Possible Forms of Combination.**—After the composition and the molecular weight of a compound have been empirically determined, the next question is to ascertain the manner in which the atoms are linked together. This is a purely mathematical problem and the answer can, when necessary, be calculated by permutations. It is obvious that any indefinite number of atoms cannot unite together to form distinct compounds: for instance, the number of monovalent atoms is limited, as each monovalent atom can only unite with one other atom, and cannot lengthen the chain to any greater extent. Compounds composed entirely of monovalent atoms can only exist in the form represented by type I. (§ 40). Compounds composed of one polyvalent atom and several monovalent atoms exhibit forms exemplified by types II. to VIII. The number of monovalent atoms which can enter into combination corresponds to the valency of the polyvalent atom. If a second or third polyvalent atom is added, then two valencies are required for the linking of each additional polyvalent atom, and are, therefore, not available for union with monovalent atoms. The number of monovalent atoms is increased by a number equal to two less than the valency of the new polyvalent atom. If n_1, n_2, n_3, n_4, represent the number of mono-, di-, tri- and tetra-valent atoms, then the maximum number of monovalent atoms will be

$$\begin{aligned} n_1 &= 2n_2 + 3n_3 + 4n_4 + 5n_5 + 6n_6 + 7n_7 + 8n_8 \\ &\quad - 2(n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 - 1) \\ &= 2 + 1n_3 + 2n_4 + 3n_5 + 4n_6 + 5n_7 + 6n_8 \end{aligned}$$

In organic compounds, which usually contain only mono-, di-, tri-, and tetra-valent atoms,

$$n_1 = 2 + 1n_3 + 2n_4.$$

The number of divalent atoms has no influence on the number of monovalent atoms. Each trivalent atom increases the number of possible monovalent atoms by one, and each tetravalent atom by two. As no compounds are known in which the number n_1 of monovalent atoms is greater than is here indicated, this is regarded as a confirmation of the theories of valency and of atomic linking.

If there is only one polyvalent atom in the molecule then only one constitution is possible, even when the monovalent atoms differ in their nature, because the valencies of one and the same atom must be held to be equivalent (§ 43), and it is, consequently, immaterial which atom is united to a given affinity. The following formulæ admit of only one interpretation:

CH_4	CH_3Cl	CH_2Br_2	$CHBr_3$	CH_2ClBr
Methane	Methylchloride	Methylenebromide	Bromoform	Chlorobromomethane

The question (§ 54) whether the formulæ only admit of one interpretation when all four monovalent elements are different is an open one, but will probably be decided in the negative. When two polyvalent atoms combine, the formula has only one meaning when all the affinities are satisfied by monovalent atoms of the same element. For example:

$C_2H_6 = H_3C--CH_3$	$CNH_5 = H_3C--NH_2$
Ethane	Methylamine

Three similar polyvalent atoms can unite with one kind of monovalent atom to form saturated compounds, which can only exhibit one form of structure, *e.g.* propane:

$$CH_3--CH_2--CH_3.$$

Again, one structure alone is possible in a compound containing two polyvalent atoms where one of the monovalent atoms differs from the others, *e.g.*:

H_3C--CH_2Cl	H_3C--CH_2I	$Cl_3C--CHCl_2$
Ethyl Chloride	Ethyl Iodide	Pentachlorethane

But this is no longer the case when a second monovalent atom of another element enters the compound. The entrance of the first of these two atoms puts an end to the equality between the two polyvalent atoms, and consequently it is now a matter of importance with which particular polyvalent atom the second monovalent atom unites. Isomeric compounds are now possible, and the number of such compounds theoretically possible are actually known. When there are only two atoms of the new kind present, it does not matter whether they are alike or dissimilar. Only two forms are possible for the compounds

$$C_2H_4Cl_2 \quad \text{and} \quad C_2H_4ClBr$$

$$H_3C - - CHCl_2 \quad \text{and} \quad H_2ClC - - CH_2Cl$$

Ethylidene chloride Ethylene chloride

$$H_3C - - CHClBr \quad \text{and} \quad H_2ClC - - CH_2Br$$

Ethylidene chlorobromide Ethylene chlorobromide

But if the number of different monovalent elements increases the number of isomerides will increase. If all six monovalent atoms are different, then there will be ten isomerides, as can be calculated by permutation. If the six monovalent atoms are numbered 1, 2, 3, 4, 5, 6, then we have the following combinations:

The first C atom			The second C atom		
1	2	3	4	5	6
1	2	4	3	5	6
1	2	5	3	4	6
1	2	6	3	4	5
1	3	4	2	5	6
1	3	5	2	4	6
1	3	6	2	4	5
1	4	5	2	3	6
1	4	6	2	3	5
1	5	6	2	3	4

or $(4+3+2+1)=10$ combinations.

In the case of three similar or two dissimilar polyvalent atoms, isomerism occurs as soon as a single atom of a second monovalent element enters the compound:

$$CNH_4Cl = CH_2Cl - - NH_2 \quad \text{or} \quad CH_3 - - NHCl$$

Chloromethylamine Methylchloramine

$$C_3H_7Cl = CH_3 - - CH_2 - - CH_2Cl \quad \text{or} \quad CH_3 - - CHCl - - CH_3$$

Propylchloride Isopropylchloride

The number of isomeric compounds increases rapidly as the number of polyvalent atoms and the variety of monovalent elements increase. Three carbon atoms and eight similar monovalent atoms can only be arranged in one manner, but if the eight monovalent atoms are all different, then no less than 280 forms of combination are possible. It is clear that the atomic linking in a given compound can only be determined by calculation in the very simplest cases.

§ 46. **Determination of the Linking by Synthesis and Analysis.** The decomposition and building up of compounds afford a valuable means of determining the atomic linking. The conclusions based on these methods depend on the assumption that those atoms which are united together before the union of two compounds remain united together after the act of combination, and that, on the other hand, those atoms which remain joined together after the decomposition of a compound were previously united in the said compound. This deduction was made use of long before the doctrine of atomic linking was known; but, strange to say, the conclusions arrived at in this way were proved to be untenable by the knowledge of atomic linking and were abandoned after a prolonged discussion.

The very ancient observation that a salt is formed from an acid and a base, and can again be decomposed into these constituents, led to the view that the acid and base are present as such in the salt. Calcium carbonate decomposes into lime and carbon dioxide, $CaCO_3 = CaO + CO_2$; from this it was inferred that calcium carbonate contained the proximate constituents CaO and CO_2, and that its formula was CaO,CO_2.

Analogous formulæ were given to other salts, *e.g.*—

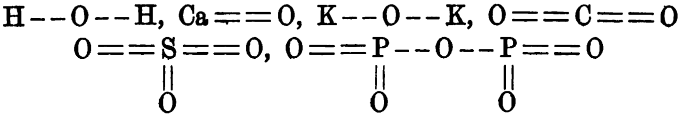
CaO,SO_3	K_2O,SO_3	$3CaO,P_2O_5$
Calcium sulphate	Potassium sulphate	Calcium phosphate

And similar formulæ were used for the acids:

H_2O,SO_3	$3H_2O,P_2O_5$
Sulphuric acid	Phosphoric acid

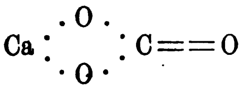
and so on.

Formulæ of this description are at present used solely for 'molecular aggregations,' such as salts with water of crystallisation. That they are not permissible for real chemical compounds is obvious from the fact that these groups are already saturated and therefore have no free affinities available for mutual combination.

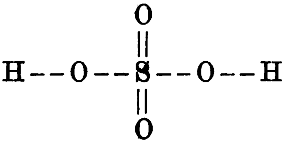


$$H{-}{-}O{-}{-}H,\ Ca{=}{=}O,\ K{-}{-}O{-}{-}K,\ O{=}{=}C{=}{=}O$$
$$O{=}{=}\underset{\underset{O}{\|}}{S}{=}{=}O,\ O{=}{=}\underset{\underset{O}{\|}}{P}{-}{-}O{-}{-}\underset{\underset{O}{\|}}{P}{=}{=}O$$

These formulæ are called dualistic, on account of their separation into two parts. They have been replaced by others in which the groups are united together by means of their oxygen atoms:



$$Ca\!:\!\begin{array}{c}.O.\\ \cdot O\cdot\end{array}\!:\!C{=}{=}O$$



$$H{-}{-}O{-}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}{-}O{-}{-}H$$

The principle underlying these old formulæ—viz. the assumption that those atoms which were united in a compound must be regarded as remaining combined—still remains in force, but in its application due care is taken to comply with the laws of atomic linking.

For example, the action of hydrochloric acid on alcohol is represented by the equation—

$$\begin{array}{ccccccc} C_2H_6O & + & HCl & = & C_2H_5Cl & + & HOH\\ \text{Alcohol} & & \text{Hydrochloric acid} & & \text{Ethyl chloride} & & \text{Water}\end{array}$$

In this case two of the carbon atoms and at least four of the hydrogen atoms remain together; we may assume, therefore, that these atoms are contained in alcohol and in ethyl chloride also—

$$\begin{array}{ccc} C_2H_4,H_2O & \qquad & C_2H_4,HCl\\ \text{Alcohol} & & \text{Ethyl chloride}\end{array}$$

The two groups H_2O, water, and HCl, hydrochloric acid, are closed groups, in which all the affinities are saturated. We must therefore assume that not more than one hydrogen atom in alcohol is united to oxygen; that is to say, that alcohol contains the monovalent 'hydroxyl' group, $—O——H$, and that this group and the five hydrogen atoms must be directly attached to the carbon thus: $C_2H_5——O——H$.

By the action of hydrochloric acid oxygen is split off; there is no doubt about this taking place, as the oxygen ceases to be united to carbon. The oxygen atom takes away with it the atom of hydrogen to which it was previously united. Where does the second atom of hydrogen come from? Is it taken away from the carbon or the chlorine? Since the monovalent chlorine must detach itself from the hydrogen before it can unite with the carbon, it is more than probable that the hydrogen atom from the hydrochloric acid combines with the hydroxyl. As there is only one interpretation for a group containing two carbon atoms, the formula must be

$$\underset{\text{Alcohol}}{CH_3{-}CH_2{-}O{-}H} + H{-}Cl = \underset{\text{Ethyl chloride}}{CH_3{-}CH_2Cl} + H{-}O{-}H$$

The groups of atoms which remain united together in these reactions are termed 'radicals,' as they were considered to be the roots from which the peculiarities of the compounds arose; this expression dates back to the time of Lavoisier. Alcohol and ethyl chloride have the same root, the radical ethyl, C_2H_5.

Further conclusions as to atomic linking may be deduced from the decomposition and the mode of formation of substances. If an atom or a radical replaces another in a compound, we assume that it takes the place previously occupied by the latter. The chlorine from the hydrochloric acid takes the place of the hydroxyl, and the hydroxyl takes the place of the chlorine and unites with the hydrogen atom. This replacement of one atom or radical by another is termed 'substitution,' and is distinguished from 'addition'—*i.e.* the simple union or combination of two radicals or atoms; *e.g.*

$$\underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Bromine}}{Br_2} = \underset{\text{Ethylene bromide}}{C_2H_4Br_2}$$

The formation of additive compounds is frequently used in determining atomic linking, it being assumed that the addition takes place at those points where the available affinities are situated.

§ 47. **Determination of Atomic Linking from Physical Properties.**—Numerous observations show that the atomic linking exercises a marked influence on the properties of substances, and it often happens that two isomeric compounds containing exactly the same constituents possess totally different properties, solely in consequence of the different linking of their atoms; *e.g.* ethyl acetate has a pleasant ethereal odour and butyric acid has a rancid, offensive smell. When the constitution of a series of substances has been investigated, the influence of the atomic linking on their properties is soon apparent, and we are now able to determine the atom linking by a study of the properties. The following physical properties chiefly come into consideration: density, fusibility, volatility, colour, solubility, crystalline form, smell, taste, physiological action. The relation of all these properties to atomic linking has not yet been sufficiently investigated. These relations grow clearer day by day, and by this knowledge it is now possible to make new substances possessing certain desired properties. The recent syntheses of dyes and colouring matters offer a brilliant example of our power to accomplish this object.

The application of physical properties to the investigation of atomic linking depends chiefly on the fact that the physical properties change regularly, when a certain definite alteration in the atomic linking is repeatedly made and the rest of the compound is left unchanged. If we examine a series of organic compounds, the members of which differ from each other in their molecular weights by increments of 1C and 2H, it is often observed that the boiling points of these bodies exhibit a certain fixed difference for each CH_2 group. This is not always the case, but only when the constitution and linking remain the same, with the exception of the slight difference in composition due to the introduction of the group CH_2. When we find that there is a regular increase in the boiling point with the molecular weight, we conclude that the bodies have the same or similar atomic linking. Numerous examples of these relations are found in the text-books on organic chemistry.

§ 48. **Determination of Atomic Linking from the Chemical Behaviour.**—The chemical properties are even more dependent on the atomic linking than the physical properties. The influence which certain groups of atoms exert on chemical behaviour is first determined in compounds of comparatively simple structure, such as those, for instance, in which only one arrangement of the atoms is possible or such as permit their atomic linking to be easily ascertained. More complicated compounds exhibiting similar properties are assumed to contain the same groups of atoms. If large or small deviations occur, the origin of these is investigated by increasing the number of observations and comparing them with one another. In this way a valuable collection of rules has been obtained, which enable us to deduce the structure of compounds from their chemical properties.

In the case of each of the frequently occurring combinations of atoms, such as hydroxyl, OH, amide, NH_2, imide, NH, &c., we have not only determined which properties of the compounds indicate their presence, but we have also ascertained the differences in their behaviour caused by the nature of the atoms or radicals with which they are combined. For example, we are not only acquainted with a whole series of tests for identifying the presence of hydroxyl, but we can also ascertain, from the peculiarities in the behaviour of the substance, whether this hydroxyl is attached to carbon or nitrogen or whether the carbon atom united to the hydroxyl is combined with hydrogen, or oxygen, or only another carbon atom. In other words, we have the means of discriminating between the following formulæ :

$$=N-OH,\ CH_2-OH,\ =CH-OH,\ \equiv C-OH,\ -CO-OH,$$

and many others.

If a compound contains nitrogen we can ascertain from its chemical character whether the nitrogen is directly combined with oxygen, oxygen and carbon, hydrogen and carbon, or with carbon only.

The relations between atomic linking and chemical properties are, at the present time, amongst the chief objects of investigation in the field of organic chemistry, and are generally discussed in connection with this branch of the science. Unfortunately this subject seldom meets with systematic and comprehensive treatment.[1]

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[1] The relationship is systematically treated in E. Lellman's *Principien der organischen Synthese*, Berlin, 1887.

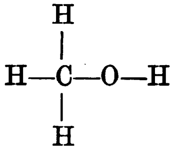
§ 49. **History of the Development of the Theory of Atomic Linking.**—Our present knowledge of atomic linking has not been gained by a peaceful, gradual development. On the contrary, in proportion as the number of organic compounds which were investigated and analysed increased, there was a corresponding growth in the number of new formulæ employed, and these formulæ were changed when they appeared no longer to answer their purpose. Much was left to individual caprice, and formulæ were used of which it is scarcely possible at the present day to discover the meaning. It is only natural that under these conditions differences of opinion were frequent, and disputes arose, which were carried on with bitterness rising in proportion as the difficulty of proving the correctness of one view or the other increased. Gradually these points of difference were smoothed away, and widely divergent views were brought into accord. At the present time all chemists, with very few exceptions, agree in recognising as correct those formulæ which have been established in accordance with the laws of the theory of atomic linking.

As a result of this gradual development, the correct expression of the composition of most substances was discovered, before the theory, on which the formulæ are based, was known. The theory is still of great value, and is used in determining the formula of every newly discovered substance; it is also useful in testing and correcting those constitutional formulæ already in use; and, finally, it forms the philosophical basis for the theories with which the experienced chemist is so familiar that he scarcely notes the foundations on which they rest, but which prove difficult for the beginner to understand if he has not received systematic instruction in these matters.

We will now study a few examples of the method pursued in determining the constitution of an organic compound.

§ 50. **Examples of the Determination of the Atomic Linking.**—We will assume that the constitution of that class of organic bodies termed 'alcohols' (from the Arabic name for spirits of wine) is unknown and has to be determined. These bodies are composed of carbon, hydrogen, and oxygen, and are characterised by certain properties common to all members of the class, more particularly by their power of reacting with acids, with elimination of water, to form ethereal salts. On hydrolysis the ethereal salts yield the original acid and alcohol. The alcohols are mono-, di-, or poly-acid, that is, they can combine with one, two, or more equivalents of an acid. The mono-acid contains at least one, the di-acid two, the tri-acid three oxygen atoms, from which we may conclude that there is a close connection between the equivalence of the alcohol and the quantity of oxygen it contains. We will confine our attention to the mono-acid alcohols, and only consider those mono-acid alcohols containing the maximum number of hydrogen atoms, which have the general formula $C_nH_{2n+2}O$, in which n may represent any whole number; its value generally lies between 1 and 30. Some of these alcohols are liquid at the ordinary temperature, others are solid but easily fusible. They are all volatile, and can be distilled: in the case of the higher members of the series the distillation must be carried on under reduced pressure. The volatility generally diminishes as the molecular weight increases, but a larger molecular weight is not always accompanied by a higher boiling point. Isomeric alcohols have, without exception, different boiling points.

In order to determine the atomic linking it is best to begin with the lowest member of the series—that is, with the member having the lowest molecular weight. This is wood spirit, CH_4O, in the formula for which $n=1$. It is obvious that only one arrangement of the atoms is possible in this case:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}O{-}H} \\ | \\ \mathrm{H} \end{array}$$

As no other mode of combination is possible, the alcohol must be a compound of methyl (CH_3) and hydroxyl (HO). This view is confirmed by the behaviour of the compound, *e.g.*

$$CH_3{-}OH + H{-}I = CH_3{-}I + HOH$$

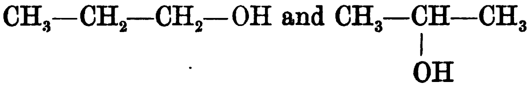
As this and analogous reactions are common to all alcohols, it is probable that they all contain hydroxyl. If $n=2$, the formula is that of spirits of wine, C_2H_6O. In this case two different modes of arranging the atoms are possible:

$$\underset{\text{Ethyl hydroxide}}{CH_3{-}CH_2{-}OH} \quad \text{and} \quad \underset{\text{Methyl oxide}}{CH_3{-}O{-}CH_3}$$

But the alcohol must have the first formula, because the radical ethyl, C_2H_5, can be expelled unchanged from this compound by the action of acids and other substances, and this shows that the two carbon atoms are united together. The second combination represents the formula of a well-known compound (methyl oxide) which may be prepared by the following reaction:

$$\underset{\text{Sodium methylate}}{CH_3{-}O{-}Na} + \underset{\text{Methyl iodide}}{CH_3{-}I} = \underset{\text{Methyl ether}}{CH_3{-}O{-}CH_3} + \underset{\text{Sodium iodide}}{NaI.}$$

There is not a second alcohol isomeric with ethyl alcohol; but when $n=3$, two isomeric alcohols are possible. Both contain the group of atoms C_3H_7, propyl; but the compounds which these two radicals form are only isomeric, and not identical. It is evident, then, that the radicals are not identical, but merely isomeric. Now, three carbon atoms can only be linked together in one way; the difference must therefore be due to the manner in which the hydrogen atoms are distributed. Taking this into account, we can only have two formulæ for the alcohols:



$$CH_3{-}CH_2{-}CH_2{-}OH \quad \text{and} \quad CH_3{-}\underset{\substack{|\\ OH}}{CH}{-}CH_3$$

The hydroxyl is either united to one of the end carbon atoms, which is also combined with two hydrogen atoms, or it is attached to the middle carbon atom, which is united to one hydrogen atom. Now the question arises, which formula is to be ascribed to each of the two known alcohols, $C_3H_7.OH$. One is formed together with ethyl alcohol in the process of fermentation, and occurs in fusel oil, and boils at 97°C.; the other boils at 83°, and was first prepared by Friedel by the action of nascent hydrogen on acetone, C_3H_6O.

If we compare these formulæ with that of ethyl alcohol we find that the formula of ethyl alcohol bears a closer resemblance to the first than it does to the second formula, for the hydroxyl is attached to a carbon atom which is united to two hydrogen atoms, and only *one* other carbon atom. It is therefore probable that the first formula belongs to that alcohol which bears the closest resemblance to ethyl alcohol.

This is without doubt the fermentation propyl alcohol boiling at 97°. Without going into detail, we may point out that, like ethyl alcohol, this alcohol on oxidation loses two atoms of hydrogen, forming an aldehyde (alcohol dehydrogenatus), and this by taking up oxygen is converted into an acid. On oxidation isopropyl alcohol, boiling at 83°, yields the acetone C_3H_6O, from which it was obtained by reduction, but it does not yield any acid. Other isomeric alcohols exhibit a similar difference of behaviour on oxidation. It is consequently important to ascertain the atomic linking of the aldehydes, acids, and acetone. The aldehydes and acids have the molecular weights represented by the following formulæ :

CH_2O	C_2H_4O	C_3H_6O
Formaldehyde	Acetaldehyde	Propionaldehyde
CH_2O_2	$C_2H_4O_2$	$C_3H_6O_2$
Formic acid	Acetic acid	Propionic acid

As these bodies are derived from alcohols, all their carbon atoms must be united together. But as the number of hydrogen atoms does not attain the maximum value for n, given in § 45, the question arises: Are we to assume the existence of unsaturated affinities or of double linking? This question is difficult to decide experimentally in the case of the aldehydes. With regard to the acids, the answer is decidedly in the negative. We consider that the hydroxyl of the alcohol remains in the acid, as it is easy to simultaneously expel from an acid one atom of oxygen and one of hydrogen. If we make use of this supposition, only one of the theoretically possible formulæ for formic acid derived from methyl alcohol is available, viz. H—CO—OH.

The radical HCO, which is combined with the hydroxyl, is called 'formyl;' it is composed of carbonyl, CO, and hydrogen, H.

On comparing this formula with that of methyl alcohol, it is seen that in addition to the hydroxyl, the acid contains an atom of oxygen attached to the carbon atom instead of two atoms of hydrogen in the alcohol. The close resemblance which exists between acetic and propionic acids and formic acid makes it highly probable that these acids are formed from the alcohols in a similar way, and contain instead of two atoms of hydrogen, one atom of oxygen, united to the carbon atom to which the hydroxyl is attached. According to this hypothesis the formulæ for the acids would probably be

Formic acid, $H—CO—OH$
Acetic acid, $CH_3—CO—OH$
Propionic acid, $CH_3—CH_2—CO—OH$

If these formulæ are correct the group of atoms termed 'carboxyl,' CO—OH, is characteristic of these acids and determines their properties. Formic acid is therefore hydrogen carboxyl ; acetic acid, methyl carboxyl; and propionic acid, ethyl carboxyl. This supposition is confirmed by the behaviour of the acids; for in reactions in which formic acid and its salts give off hydrogen, acetic acid yields methyl and propionic acid yields ethyl.

All three acids are decomposed by heating with an excess of caustic soda, yielding sodium carbonate and hydrogen, methyl hydride or methane, ethyl hydride or ethane respectively.

$$H—CO—ONa + HONa = H—H + NaO—CO—ONa$$
$$CH_3—CO—ONa + HONa = CH_3—H + NaO—CO—ONa$$
$$C_2H_5—CO—ONa + HONa = C_2H_5—H + NaO—CO—ONa$$

These views are confirmed by many reactions of these acids, and the investigation of many other acids proves that wherever the carboxyl group of atoms occurs the compound has the properties characteristic of an acid.

When this was once recognised it became evident why some alcohols do not yield acids. Only those alcohols can yield acids which contain a carbon atom, which is united to two hydrogen atoms and the hydroxyl group.

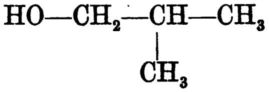
The group $-CH_2-OH$ is as characteristic of these 'primary' alcohols (as they are called) as the carboxyl group is of the acids.

In the same way it can be shown that the group $=CH-OH$ is characteristic of the second class, the 'secondary' alcohols, which yield acetone or kindred bodies on oxidation. The 'tertiary' alcohols which yield neither acids nor ketones, but lose carbon on oxidation, contain the group $\equiv C-OH$.

After ascertaining these characteristic points of difference for a large number of alcohols, the other chemical and physical properties of the alcohols are investigated. The results show that, in a group of isomeric alcohols, the primary boil higher than the secondary, and these again higher than the tertiary, but in the case of solid isomeric alcohols, the tertiary have the highest melting point. The three classes of alcohols can be distinguished by means of their boiling points. Although it is unnecessary to use this method for this particular purpose, it proves of great value in discriminating between isomeric alcohols of the same class. For example, four isomeric butyl alcohols ($C_4H_{10}O$) are known; two of these are primary, and consequently contain the group $HO-CH_2-$. The difference between them must consist in a difference in the arrangement of their other carbon atoms. According to theory, two modes of linking are possible:

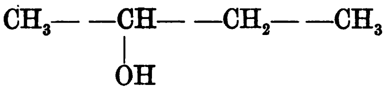
$$HO-CH_2-CH_2-CH_2-CH_3$$

and



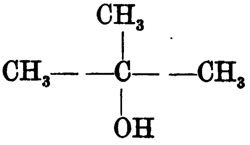
$$HO-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

Which of these formulæ belongs to the alcohol boiling at 116°, which is obtained by the reduction of butyric acid, and which formula must be ascribed to the alcohol boiling at 109° and contained in fusel oil? This problem may be solved in different ways. By depriving each alcohol of the elements of water a hydrocarbon, butylene (C_4H_8), is obtained. Each butylene unites with hydriodic acid, forming a butyl iodide (C_4H_9I), in which the iodine can be replaced by hydroxyl. The original alcohols are not reproduced by this process. The alcohol boiling at 116° yields a secondary alcohol (boiling point 99°), and the alcohol boiling at 109° yields a tertiary alcohol boiling at 83°. Only one formula is possible for each of these alcohols:



$$CH_3{-}{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}{-}CH_2{-}{-}CH_3$$

Secondary



$$CH_3{-}{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}{-}{-}CH_3$$

Tertiary

The difference from the original alcohols can only be due to the fact, that the new hydroxyl does not take up the position previously occupied by the old hydroxyl. Imagine that they are reconverted into primary alcohols, then we get the preceding formulæ again, and we see that the first formula, in which no carbon atom is directly united to more than two others, belongs to the alcohol boiling at 116°; the other, in which one carbon atom is united to three others and one hydrogen atom—is consequently in a 'tertiary' position —belongs to the alcohol boiling at 109° obtained from fusel oil. The first kind of linking is termed 'normal' to distinguish it from the abnormal 'branched' or 'side-chain' linking.

Experience has shown that the normal compounds always have a higher boiling point than those with side chains, and that the boiling point of the latter falls as the number of side chains increases. In the case of bodies having a similar constitution, the addition of CH_2 raises the boiling point from 18° to 22°. This fact may be used for determining the constitution or for testing and confirming the accuracy of a constitution determined by other methods.

§ 51. **Aromatic Compounds.**—Benzene and the so-called aromatic compounds[1] derived from it offer a remarkable example of the manner in which the atomic linking has been investigated. Benzene is a hydrocarbon which contains the same number of carbon and hydrogen atoms. Its composition is represented by the formula C_nH_n, where n stands for a whole number. Its molecular weight is therefore

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[1] The name 'aromatic compounds' has its origin in the fact that the members of this group which were first investigated possess an aromatic odour, a property not shared by all the members.

$$m = n\ (\mathrm{C} + \mathrm{H}) = n\ (11{\cdot}97 + 1) = n \times 12{\cdot}97.$$

Faraday found that the density of its vapour is 2·752 times that of air ; m will therefore be approximately 79·43.

$$m = 28{\cdot}87 \times 2{\cdot}752 = 79{\cdot}43,$$

or, for the corrected value,

$$m = 6 \times 12{\cdot}97 = 77{\cdot}82 = C_6H_6.$$

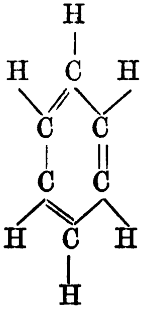
A very large number of combinations is possible for the twelve atoms contained in such a molecule, and, at first sight, it appears perfectly hopeless to attempt to investigate the constitution of benzene.

An ingenious interpretation of the behaviour of this substance led Kekulé to propose an hypothesis which explains all its peculiarities in the simplest way. This hypothesis has maintained its position to the present day, in spite of all the criticism to which it has been exposed for a quarter of a century. The hypothesis is based on the observation that, when an atom of hydrogen in benzene is replaced by another atom or radical, only one single derivative is produced. It does not matter which of the hydrogen atoms is replaced ; isomeric compounds are never formed. That it is not always one and the same hydrogen atom that is replaced, but that in reality different hydrogen atoms are displaced, can be shown in the following way. Nitro-benzene is formed by the action of nitric acid on benzene :

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Nitric acid}}{HO{-}NO_2} = \underset{\text{Nitro-benzene}}{C_6H_5{-}NO_2} + \underset{\text{Water}}{H_2O}$$

Chloro-benzene (C_6H_5Cl) can be prepared in several ways from this nitro-benzene, in which the nitro- group (NO_2) has replaced an atom of hydrogen. We may either reduce the nitro- group to NH_2 and replace the latter by chlorine, or we may replace a hydrogen atom in nitro-benzene by chlorine (in this case it is evident a different hydrogen must be displaced). The nitro- group is eliminated from the chloro-nitro-benzene

($C_6H_4NO_2Cl$) and replaced by hydrogen. Experiments of this kind have been conducted in widely different forms, but they all yield one and the same chloro-benzene. From this behaviour of benzene we conclude that all the hydrogen atoms in benzene are equivalent to one another in every respect, and that each hydrogen atom is combined in exactly the same way as each of the others. These conditions are satisfied by Kekulé's hypothesis that all six carbon atoms are united together forming a closed ring,[1] and the hydrogen atoms are uniformly distributed amongst the carbon atoms as is shown by the following formula :



In order that all four affinities of each carbon atom may come into play, it is assumed that the linking in the ring is alternately by one and by two affinities. In recent times this comparatively minor detail of the hypothesis has given rise to much discussion.

Kekulé's formula explains the whole behaviour of benzene and its derivatives in a remarkably satisfactory manner. In the first place it indicates that each 'mono-substitution product' obtained by the replacement of one of the hydrogen atoms can exist in one form only, and that isomerides cannot exist. But if a second atom or radical is substituted for a hydrogen atom, the perfect symmetry of the molecule is changed, and the second atom may take one of three positions, namely, next to the first or separated from it by one or by two carbon atoms. If the first atom takes the position at

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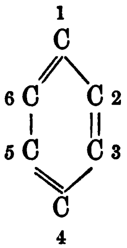
[1] The ring formula does not indicate that the atoms are arranged in a plane circle, but only that they form a closed chain.

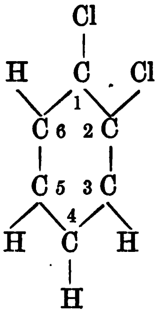
1, the second may occupy the position at 2 and 6 (which are identical), or at 3 and 5, or finally at 4.



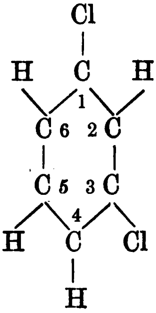
Strictly speaking, the positions 2 and 6 are not absolutely identical on account of the double linking; this has led some authors to assume that the fourth affinities are free or else united to the opposite carbon atoms. These modifications of the hypothesis have not up to the present acquired any particular practical significance.

In spite of the repeated endeavours of many chemists to discover four isomeric di-substitution products of benzene, *e.g.* di-chloro-benzenes, not more than three have ever been discovered. It is this circumstance which has gained for Kekulé's hypothesis a general recognition of its value. The three isomeric di-substitution products are distinguished by the prefixes 'ortho,' 'meta,' and 'para.'

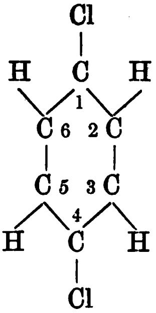
The problem now arises, Which of the three positions 1 . 2, 1 . 3, and 1 . 4, or which of the three formulæ



1 . 2 or 1 . 6



1 . 3 or 1 . 5



1 . 4

is to be assigned to each of these compounds?

Owing to the inherent difficulties of the problem, this question was debated for years, and our views on the subject have undergone frequent change. One remarkable fact is, that on further substitution the para- derivative only yields one tri-substitution product, but both of the other derivatives yield more than one tri-substitution product. As it is only in the third formula that the four remaining hydrogen atoms occupy similar positions, this formula has been assigned to the para-compounds 1 . 4. In the first formula, 1. 2, the four remaining hydrogen atoms are in two different positions to the chlorine atoms, 3 and 6 are adjacent to the chlorine atoms, 4 and 5 are separated from them by a carbon atom. In the second formula, 1 . 3, the third chlorine atom may occupy three different positions—*e.g.* 2, between the two chlorine atoms; 4 and 6, adjacent to the chlorine atoms; and 5, separated by a carbon atom. As it has been proved by experiment that an ortho-di-substitution product can only yield two tri-substitution products, and the meta-compound yields three tri-substitution products, the formula 1 . 2 is assigned to the ortho- and 1 . 3 to the meta- derivatives.

Numerous comparisons have fully confirmed these hypotheses, and since the year 1874 the accuracy of these views has not been disputed.

These examples suffice to give an idea of the methods by which our intimate knowledge of the constitution of organic compounds has been acquired.

We may see in this a confirmation of the saying of Bacon:

> Nec manus nuda, nec intellectus sibi permissus ad inveniendam veritatem multum valet. Instrumentis et auxiliis res perficitur, quibus opus est non minus ad intellectum quam ad manum.

§ 52. **Physical Isomerism. Allotropy.**—As the investigation of the constitution of organic compounds was extended, many instances were observed in which a larger number of isomeric bodies were discovered than could be accounted for by means of the formulæ derived according to the laws of atomic linking. In most of these cases the isomeric substances differed less in their chemical than in their physical properties, such as density, melting point, crystalline form, &c.

Such cases of isomerism which could not be explained by chemical formulæ were termed 'physical isomerides' to distinguish them from the 'chemical isomerides,' which are caused by a difference in the mode of linking. This physical isomerism is very closely related to and is almost identical with 'allotropism.' The latter expression was introduced by Berzelius, and applied by him to describe the occurrence of elements in different forms or conditions, or 'allotropic modifications.' Before the molecules of elementary bodies were regarded as compounds of similar atoms, the existence of one and the same element in different modifications could not be explained in the same way as the isomerism of compounds. Hence the necessity of a special term to be applied to this class of phenomena. At the present time the expression 'allotropism' is also applied to compounds, and is synonymous with physical isomerism. There are several kinds of physical isomerism.

§ 53. **Polymorphism.**—Dimorphism and polymorphism are common forms of physical isomerism. When one and the same substance crystallises in two or more distinct forms, it is said to be dimorphous or polymorphous. Both elements and compounds exhibit this peculiar phenomenon. Well-known examples of polymorphism are exhibited by carbon, which crystallises in the regular system as the diamond, and in the hexagonal system as graphite. Sulphur is deposited from fusion in monoclinic crystals and from solution in carbon bi-sulphide in rhombic crystals. Calcium carbonate ($CaCO_3$) occurs in rhombohedral crystals as calcite and in rhombic crystals as arragonite. Silica is met with in two distinct hexagonal forms as quartz and tridymite. Titanium dioxide (TiO_2) exists in three distinct forms as rutile, brookite, and anatase. Stannic oxide (SnO_2), which is isomorphous with titanium dioxide, assumes the same forms as rutile and brookite, and perhaps anatase. These bodies are consequently 'isodimorphous' or 'isotrimorphous.'

There are many other examples of isodimorphism, such as that of the oxides of arsenic and antimony, As_4O_6 and Sb_4O_6, the sulphides of copper and silver, Cu_2S and Ag_2S. Many organic compounds are also dimorphous.

The form that a di- or poly-morphous body assumes on crystallisation depends chiefly on the temperature, and also on certain other external conditions. If the crystallisation takes place from a solution, the nature of the solvent, the presence of other substances, especially of such as are isomorphous with one of the forms of the body in question, influence the form that body assumes.

The conditions under which many forms are produced are entirely unknown. We do not know under what conditions carbon crystallises as diamond, in spite of the numerous attempts which have been made to produce this valuable gem.[1] In the case of many organic compounds one modification has been accidentally obtained, but the conditions under which it is formed still remain unknown.

The allotropic modifications of a substance differ considerably in their stability. Some modifications when once formed are very stable, but others can only exist within narrow limits of the conditions under which they are produced. As examples of the first class we have carbon as diamond or graphite; sulphur is an example of the second class.

The diamond and graphite can exist unaltered side by side, and it is only at a very high temperature that the diamond is converted into graphite. On the other hand the rhombic form of sulphur is only stable below, and the monoclinic form above, a temperature of 95°·6 C.; both modifications can exist unchanged for some time outside these limits. But they are in a state of unstable equilibrium, which is easily upset by heating, or shaking, or more particularly by contact with a crystal of that modification which is stable at the prevailing temperature, when the whole mass is converted into this form.

Many dimorphous organic compounds behave like sulphur in this respect, and as a rule only one modification is stable, and the other unstable above and below a certain definite temperature.

This kind of physical isomerism is supposed to be due to a difference in the arrangement of the particles or molecules, which are in themselves identical. The accuracy of this hypothesis cannot be proved, as we do not possess any method by which the nature, or even the size, of the molecules of solid bodies can be ascertained. But when we see that under suitable conditions crystals of both modifications can be obtained from one and the same liquid, it seems probable that these modifications are composed of similar molecules, just as different kinds of buildings can be constructed from the same kinds of bricks. This class of isomerism may be termed 'isomerism of aggregation.'

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[1] Moissan obtains diamonds by dissolving carbon in molten iron and cooling under high pressure.

§ 54. **Physical Isomerism of the Molecules.**—There are also cases of physical isomerism caused by a difference in the molecules. The examples of real polymerism belong to this class, *e.g.* when a body has different molecular weights in the gaseous and liquid states. In the case of sulphur the molecules at temperatures near the boiling point consist of six atoms, S_6, which are split up at higher temperatures into molecules consisting of two atoms, S_2. Many organic and inorganic compounds—such as certain aldehydes, acetic acid, nitrogen peroxide, &c.—exhibit analogous behaviour.

The allotropic modifications of phosphorus are probably due to differences in the number of atoms composing the molecules. If phosphorus be heated above 210° in a closed vessel too small to permit the element being completely converted into vapour, it passes from the gaseous state into a red solid modification, from which the colourless variety is regenerated, if sufficient space be offered for complete volatilisation. The red modification is produced from the compressed and the colourless from the expanded vapour at the same temperature (210–300°). It is therefore probable that both modifications already existed in the state of vapour as isolated molecules. A difference in the vapour can only be due to a difference in the molecules. It is not yet known whether this difference is to be ascribed to polymerism.

§ 55. **Optical Isomerism.**—The most remarkable form of isomerism is that in which the isomeric bodies crystallise in forms which are identical in all their individual parts, such as angles and faces, and are symmetrical but not superposable, and bear the same relation to each other that an object bears to its reflected image in a mirror, or that a right-hand glove bears to a glove for the left hand. This peculiar behaviour is generally associated with another remarkable property, viz.

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the bodies are optically active. One turns the plane of polarised light to the right, to the same extent that the other does to the left. The bodies thus acting on polarised light are divided into two classes. Some substances are optically active only when they are in a solid and crystalline state; others are optically active as liquids, either in solution or in a molten state; and a few gases or vapours are optically active. The members of the first class either crystallise in the regular form or are uniaxial and crystallise in the quadratic or hexagonal systems. If the two kinds of crystals are placed in parallel lines it is noticed that certain hemihedral faces which occur on the right side of the one set of crystals are found on the left side of the other crystals.

Cinnabar, quartz in the form of rock crystal, chlorates, bromates, periodates, thiosulphates, sodium sulphantimoniate, and some organic bodies belong to this class.

As the rotation of light by these substances depends on their crystalline form and ceases when the substances are brought into the liquid state by fusion or by solution, it is evident that the rotation is not due to the nature of the molecules, but is caused by a peculiarity in their arrangement. It is assumed that the molecules are arranged in a spiral form, and that in one form of crystal the spiral turns to the right and in the other to the left.

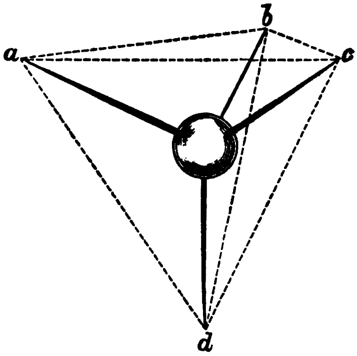
The second class of optically active compounds exhibits this property in the liquid state. In these cases the molecules are free to move about and do not take up fixed positions. Hence it appears that the rotation of light is not due to the relative position of the molecules, but to their peculiar nature.

Of course this does not exclude the possibility of these substances (if they are capable of crystallising) exhibiting a peculiar arrangement of the molecules. This is indeed the case with many compounds; *e.g.* tartaric acid ($C_4H_6O_6$) crystallises in two different forms, which are non-superposable and bear the same relation to each other that an object does to its reflected image. Only a few of these compounds crystallise in the regular system (amylamine alum) or are optically uniaxial (strychnine sulphate): these bodies rotate the plane of polarised light in the crystalline state.

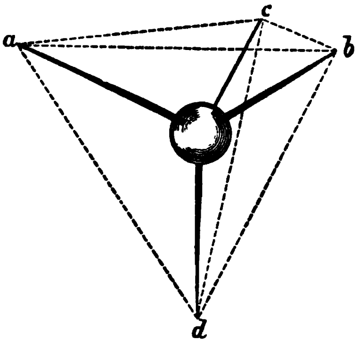
Most of these substances belong to the rhombic, monoclinic, or triclinic systems, and form optically biaxial crystals, which do not exhibit the phenomenon of rotation.

§ 56. **Asymmetrically linked Carbon Atoms.**—In investigating the cause of the rotation of light due to the nature of the molecules, it is important to notice that this peculiar phenomenon is only observed in organic compounds, and only exhibited by a comparatively small number of carbon compounds. This observation led to the hypothesis that the phenomenon is due to a peculiarity in the linking of the atoms. In fact, in 1874 two different investigators, Van t' Hoff and Le Bel, independently discovered the connection existing between the rotation of light and atomic linking and offered a perfectly satisfactory explanation of this optical isomerism.

I



II

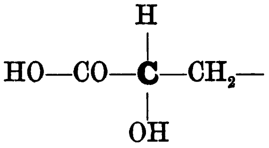


As stated in § 43, the four affinities of a carbon atom are symmetrically arranged in space, and consequently the four atoms united to the carbon atom are arranged round it like the four corners of a tetrahedron round its centre. If these four atoms all differ from each other either in their nature or in being combined with different atoms, then two forms of combination are possible. These are sketched in perspective and numbered I and II.

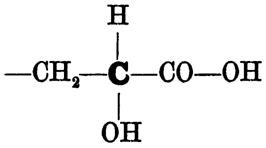
The four atoms or radicals, *a*, *b*, *c*, *d*, are attached to the carbon atom in such a way that the two figures are non-superposable, and one is the reflected image of the other. Imagine your eye is placed in the position of one of the atoms, say *a*, and directed towards the other three atoms; then it sees *b c d* in I in the direction in which the hand of a clock moves, but in II in the reverse direction.

A carbon atom in this condition is said to be an unsymmetrically linked carbon atom, or briefly an asymmetric carbon atom. A careful examination of all those compounds which in the liquid state can rotate polarised light shows that each of these bodies contains at least one asymmetric carbon atom; several contain more than one. The property of rotation depends on the presence of an asymmetric carbon atom.

Let $a = \mathrm{H}$, $b = \mathrm{HO}$, $c = \mathrm{COOH}$, $d = \mathrm{CH_2}$; these groups are contained in malic and tartaric acid: both of these acids exist in two symmetrical forms.

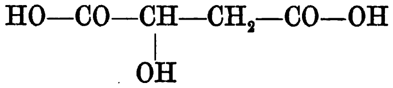


$$\mathrm{HO{-}CO{-}}\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{OH}}{\mathbf{C}}}\mathrm{{-}CH_2{-}}$$



$$\mathrm{{-}CH_2{-}}\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{OH}}{\mathbf{C}}}\mathrm{{-}CO{-}OH}$$

According to the formulæ generally in use, only one form of malic acid is possible, viz.—



$$\mathrm{HO{-}CO{-}}\underset{\displaystyle \mathrm{OH}}{\mathrm{CH}}\mathrm{{-}CH_2{-}CO{-}OH}$$

But if we take into consideration the fact that the carbon atom attached to the HO group is asymmetric, then two formulæ are possible. Starting from the hydroxyl, the sequence of the other atoms or radicals is in the direction of the hands of a clock in one formula—

$$\mathrm{H, CO{-}OH, CH_2{-}CO{-}OH}$$

and in the reverse direction in the other—

$$\mathrm{H, CH_2{-}CO{-}OH, CO{-}OH.}$$

The two formulæ are non-superposable.[1]

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[1] To make this point perfectly clear, divide the surface of two wooden balls of the same size into eight equal spherical triangles or quadrants by means of three circles cutting each other at right angles. Bore a hole down to the centre of the globe in the middle of each alternate quadrant. Insert four rods of equal length, one in each hole: these indicate the direction of the

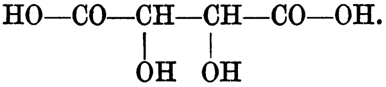
§ 57. **Active and Inactive Forms.**—The rotatory power of a compound ceases when the asymmetric carbon atom disappears; for example, malic acid is converted by reduction into succinic acid—

$$HO—CO—CH_2—CH_2—CO—OH$$

which is inactive.

The rotatory power also ceases when equivalent quantities of both modifications unite and crystallise together. For example, the two optically active malic acids unite and form an inactive acid because the rotatory power of the one neutralises that of the other. In such cases the components may be separated by means of suitable agents; for example, one constituent may combine more readily with other dextrogyrate bodies; the other may unite more easily with other lævogyrate compounds. We are acquainted with two optically active malic acids which unite together, forming an inactive modification.

If a compound contains two asymmetric carbon atoms which are united to similar atoms or radicals, then there can exist two optically active and two inactive forms. This is the case with tartaric acid; we have dextro- and lævo-tartaric acid.



$$HO—CO—\underset{OH}{\underset{|}{CH}}—\underset{OH}{\underset{|}{CH}}—CO—OH.$$

One inactive acid (racemic) is a compound of the two active forms, but the second acid owes its inactivity to the fact that the position of the other atoms attached to one carbon atom is unsymmetrical with the dextrogyrate and at the other carbon atom unsymmetrical with the lævogyrate modification.

This second form cannot be split up into two active modifications. If the two asymmetric carbon atoms are united to different atoms and radicals, the effect of one is not, as a

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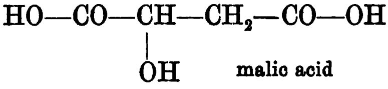
forces of affinity. Fix four balls of different colours to the free ends of the rods, and you have a representation of an asymmetrical carbon atom. According to the sequence of the coloured balls, the groups will be either identical or symmetrical, *i.e.* the reflected image of each other.

rule, counterbalanced by that of the other, and consequently all four modifications may be optically active, but in different degrees.

The number of possible isomerides increases with the number of asymmetric atoms. A large number of isomerides can exist in the series of sugars, and the terpene derivatives.

§ 58. **Physical Isomerism, with Double Linking.**—When an asymmetric carbon atom loses one of the four atoms or radicals with which it is combined, and attaches itself to a neighbouring atom by a double linking, the optical activity of the compound is lost, but the possibility of physical isomerism still continues. Malic acid ($C_4H_6O_5$) affords one of the best known examples of this kind. It loses water ($HO + H = H_2O$), forming the isomeric, fumaric, and maleic acids ($C_4H_4O_4$). The latter again loses water, yielding the anhydride $C_4H_2O_3$, but fumaric acid does not form an anhydride. There is only one formula[1] for the two acids in the system in general use, viz.



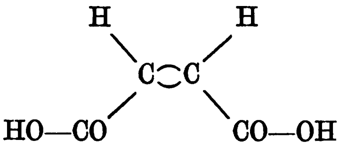
$$HO—CO—\underset{\textstyle OH}{\underset{|}{CH}}—CH_2—CO—OH$$

malic acid

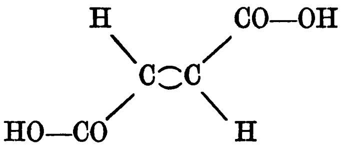
$$HO—CO—CH{=}CH—CO—OH$$

Fumaric and maleic acids

But if we take into consideration the arrangement of atoms in space, then we have two different formulæ,



Maleic acid



Fumaric acid

which Van t' Hoff and Wislicenus have shown are perfectly

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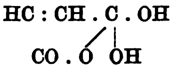
[1] The only other formula, $HO—CO—\underset{\|}{C}—CH_2—CO—OH$, cannot be correct, as fumaric and maleic acid unite with Br_2, forming one and the same dibromosuccinic acid, $HO—CO—CHBr—CHBr—CO—OH$. The discussion of the formula

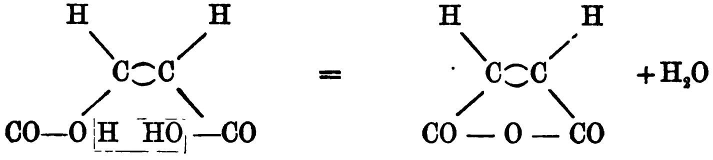


$$HC : CH . \underset{\textstyle OH}{\underset{|}{C}} . OH \quad CO . O$$

proposed by R. Anschütz is deferred.

capable of explaining the difference in the behaviour of the two acids.

It is obvious that the first formula represents maleic acid, as the proximity of the carboxyl groups —CO—OH facilitates the formation of an anhydride.

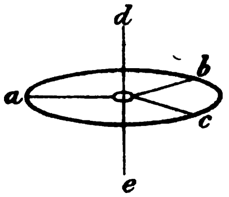


In fumaric acid the carboxyl groups are diametrically opposite each other.

Both acids combine with the elements of water, forming inactive malic acid, which can be split up into two optically active isomerides. The addition of the elements of water takes place in each of the two possible ways.

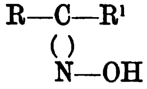
The development of stereochemistry (from στερεός)—that is the introduction of the idea of a difference in the arrangement of the atoms in space into the constitutional formulæ of organic compounds—has provided a satisfactory explanation for numerous cases of isomerism which formerly could not be accounted for. It has also led to the discovery of numerous relations between the arrangement of the atoms and the properties of compounds. The hypothesis of asymmetrically linked carbon atoms was first propounded in 1874, and it now ranks as one of the most firmly established of the doctrines of chemistry.

Recently allotropic modifications of certain nitrogen compounds have been discovered and investigated by Hantzsch and others. The cause of the difference of the two stereo-isomeric forms is probably due to the existence of the group ⊃C⊃N—OH.

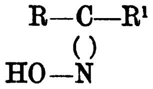


Nitrogen is pentavalent, and as it is impossible to arrange five points symmetrically in space (§ 43), it is probable that the five affinities are not exactly alike. We may consider that the lines of force of three of the affinities *a b c* lie in one plane, inclined to each other at angles of 120°, but the other two, *d* and *e*, are at right angles to this plane.

If *b* and *c* are united to carbon then the hydroxyl can occupy two different positions—viz. *d* or *e*.



$$\begin{array}{c}\mathrm{R{-}C{-}R^1}\\ (\,)\\ \mathrm{N{-}OH}\end{array}$$



$$\begin{array}{c}\mathrm{R{-}C{-}R^1}\\ (\,)\\ \mathrm{HO{-}N}\end{array}$$

In the first case the hydroxyl is near the radical R^1, in the second it is nearer R. If the OH is at *a*, R and R^1 are equidistant.

§ 59. **The Absolute Dimensions of Molecules and Atoms.**—The molecules, the constitution of which has been discussed in the preceding paragraphs, are not infinitely small, although much smaller than any magnitude perceptible to our unaided or even to the aided senses. As to the magnitude of the molecules themselves, it is at present impossible to give any exact determinations; still the limits within which the dimensions must lie can be approximately determined. Such approximations may, as was shown by Sir William Thomson in 1871, be arrived at by the aid of various physical phenomena; his conclusions have been confirmed and extended by other investigators. From certain optical phenomena—for instance, from the dispersion accompanying the refraction of light—it may be concluded, with some degree of probability, that the molecules of transparent materials, such as glass, water, and the like, are greater than the ten-thousandth part of a wave-length of light, which latter amounts again to only a few ten-thousandth parts of a millimetre. Similar conclusions may be drawn also from the diffusion of colouring matters on solution, and again from the contact electricity of metals, and the heat produced by the attraction of metallic plates oppositely electrified, from the minimum thickness which soap bubbles can attain without bursting, and especially from the properties of gases and of the liquids produced by their condensation.

The highly developed kinetic theory of gases shows, for instance, that certain relationships exist between the dimensions of gaseous particles, their velocity, and the path which they traverse before they come in contact with one another. From these relationships approximations may be made as to the weight and the mass of the molecules, and at the same time also of the atoms.

All these investigations have proved with approximate agreement that the diameters of the molecules of different substances are smaller than the ten-millionth part of a millimetre, but at the same time not indefinitely smaller than this.

§ 60. **Aggregation of the Molecules.**—Although the affinities of the atoms in a molecule are satisfied by union with each other, the total affinity, that is to say the molecule, still exerts an appreciable attraction for other molecules, for it is only by the aggregation of molecules that the particles of matter of which our senses are cognisant are produced. According to the foregoing speculation, enormous numbers of these molecules must be present even in the smallest visible and ponderable particle.

The mode of aggregation of these molecules must vary, and these differences will give rise to the different states of matter. In the solid condition the particles are held together in an unalterable position; in the liquid state they are so held that the particles move easily among one another in such a manner that no two particles remain neighbours for any length of time. Between these two conditions, forming as it were the passage between the extremes, we have the soft, plastic, and viscous states of matter in which the particles may move with greater or less difficulty, under the influence of the force of gravity or pressure, without destroying the continuity of the whole mass.

In the gaseous state the attraction of the particles for one another ceases, so that these separate particles move away into space unless they are prevented from doing so by impassable boundaries.

§ 61. **The Effect of Heat.**—In no one of these conditions can we assume that the particles are in a state of absolute rest; we must rather imagine that in each one the particles possess a certain motion, which is perceptible to us as heat, and this movement becomes the more active the greater the amount of heat the bodies take up. The form of this motion is not fully understood; still in the solid state each particle can only move round a certain fixed position of equilibrium, this motion being either vibratory or rotatory.

In liquids the particles must be imagined as moving over one another, so that they leave no spaces between them, whereas in the gaseous or vaporous condition each particle is separated from the others, and moves rapidly in a straight line until it comes in contact with some hindrance by which it is diverted from its path. A consequence of an accelerated motion of the particles is to be found in the expansion of bodies by heat, because more space is required for these extended movements.

It is, however, a remarkable fact that in the passage from one state of aggregation to another bodies take up the heat which disappears as such, so that it is no longer recognised by the senses or by the thermometer. This so-called latent heat serves, doubtless in a great part, to produce those movements of the particles which are characteristic of the new condition; in part, perhaps, also to overcome the forces of attraction between the particles, assuming such forces to exist.

The expansion exhibited by the majority of substances in melting may also be attributed to the increase of these internal movements.

In addition to the motion of the molecules we must also assume that the atoms constituting these molecules are likewise in a state of motion, and this again would be altered by the application of heat. In monatomic molecules, consisting only of one atom, as, for instance, in the case of the molecule of gaseous mercury, which has been proved to be monatomic by Kundt and Warburg, such atomic movements will not occur.

§ 62. **Homogeneous Solid Bodies.**—When similar molecules collect together to form a solid aggregate, a solid body is produced, which will have a structure determined entirely by the relative position of the particles. In the formless, or amorphous, condition the arrangement of the particles would be similar in each direction throughout the mass of the body, whilst in the case of crystals in certain directions it would be found to be different from others, and these differences are perceptible not only in the plane surfaces forming the external boundaries of the crystals, but also in any fragment taken from any part of the interior of the crystal. These differences are shown in the cohesion, the hardness, the cleavage of the crystals in certain directions, the expansion by heat, the conduction of heat, the velocity and refraction of light, the colour of the same, and in some cases also in certain peculiar electrical phenomena produced by heating or cooling. Such differences can only find their explanation in a different arrangement of the molecules. We may assume that the molecules are brought nearer together in one direction than they are in another; but the reason for such an arrangement of the molecules must be sought for in the molecules themselves; so we must assume that the particles arrange themselves together, so that their axes are parallel to one another or are otherwise regularly arranged.

The systematic disposition of points in space has been geometrically investigated by Leonard Sohncke, and its relation to the different systems of crystals established. The greater the symmetry of the distribution of such points, the simpler is the crystal system; and in full accord with this it is found that substances of the simplest composition, as, for instance, the elements and the compounds composed of a few atoms, form, as a rule, crystals belonging to the regular and hexagonal systems; whereas molecules composed of many atoms—for instance, the majority of organic compounds—yield aggregates which crystallise with little or no evidence of symmetry. In amorphous substances the particles must be imagined as arranged irregularly, for this is the only way in which the particles could be arranged so that in any finite mass all sections would be the same. In many of their properties, *e.g.* behaviour with polarised light, amorphous bodies resemble the substances crystallising in the regular system; but this is not the case for other properties, such as cohesion, hardness, and cleavage.

§ 63. **Heterogeneous Solid Molecular Aggregates.**—A solid body may also be produced by the grouping together of different kinds of molecules. Many substances crystallise with water of crystallisation; still these compounds would appear rather to be homogeneous aggregates, for every molecule is united with a definite number of molecules of water, and the molecules so produced are regularly grouped into new and larger ones. A few only of the compounds containing water crystallise in the regular system: as, for instance, the alums, the twenty-four molecules of water being so arranged around the salt molecule as to produce an aggregate homogeneous in all directions. The so-called double salts are similarly constituted to the compounds containing water of crystallisation, and these must be reckoned amongst the homogeneous aggregates, and also all other combinations produced in accordance with the laws of stœchiometry.

The mixed crystals of isomorphous bodies in which the constituents occur in varying and changing proportions must, on the other hand, be considered as heterogeneous aggregates. Thus, for example, the so-called vitriols—that is, the hydrated sulphates of magnesium, copper, zinc, iron, manganese, nickel, and cobalt—may crystallise together in any proportions. This is true also of other isomorphous substances. This crystallisation together takes place only when the compounds are of analogous constitution, and when the isomorphous constituents take up approximately the same space. If this condition is not exactly satisfied, then an angle of the crystal of one substance would be altered to a greater or less extent by the entrance into that crystal of another body. For instance, calcspar ($CaCO_3$) crystallises in rhombohedra, the angle being 105° 5′, whereas magnesite ($MgCO_3$) crystallises in the same form, the angle of which is 107° 25′. When both crystallise together in the form of dolomite the angle is 106° 15′. This difference in angle of these crystals arises from the fact that the quantity of calcium carbonate represented by its formula occupies a greater space than the quantity of magnesium carbonate represented by its formula, and the increase of volume in consequence of this results in an extension of the crystal along its chief axis.

The expansion of the crystal by heat takes place chiefly in this same direction, and brings about also a reduction of the terminal angle of the crystal.

In addition to these mixed crystals there are also amorphous heterogeneous aggregates, which are produced by the solidification of a mixture in a molten state.

§ 64. **Density of Solid Bodies.**—Great variations are exhibited by the densities of solid bodies; substances are known, *e.g.* certain metals, which are forty times as heavy as the lightest known solid, and more than twenty times as heavy as an equal bulk of water, the usual standard of comparison for solids. The apparent irregularities observed in the densities of various solids to a large extent disappear and certain regularities become apparent when the volumes occupied by the molecular weights or the stœchiometric quantities represented by their formulæ are considered, as has already been done in the case of the elements in § 36. Investigations of this kind have been carried out by H. Kopp, H. Schroeder, Traube, and others.

The inexactitude of the determinations, and also the doubts as to the temperature at which the determination should be made, have combined to retard the realisation of the laws to which these quantities are doubtless subservient.

The simplest way of looking at this problem is to compare the space occupied by a compound with that filled by the constituent elements in the free state. When this is done it is found, as a rule, that the volume of the compound is approximately equal to the sum of the volumes of the constituent elements.

According to the table in § 36, the volumes of zinc and sulphur are—

$$V\,(Zn) + V\,(S) = 9{\cdot}1 + 15{\cdot}7 = 24{\cdot}8.$$

The volume of the compound zinc sulphide formed by the union of these elements is obtained by dividing the stœchiometric quantity ZnS by the density of zinc sulphide (blende), thus:

$$V\,(ZnS) = \frac{Zn + S}{d} = \frac{65{\cdot}1 + 31{\cdot}98}{4{\cdot}05} = \frac{97{\cdot}1}{4{\cdot}05} = 24{\cdot}0.$$

Thus it is seen that the volume of the compound is approximately equal to that of the sum of the constituents. Other monosulphides show the same relation, as is exhibited in the following table, in which under the sign Σ the sum of the volumes of the constituents are given for the sake of comparison :

	Σ	Difference	V(S) calculated
$V\ (\mathrm{MnS}) = \frac{86{\cdot}8}{4{\cdot}0} = 21{\cdot}7$	22·6	−0·9	14·8
$V\ (\mathrm{FeS}) = \frac{87{\cdot}9}{4{\cdot}8} = 18{\cdot}3$	22·9	−3·6	11·1
$V\ (\mathrm{NiS}) = \frac{90{\cdot}6}{4{\cdot}6} = 19{\cdot}7$	22·4	−2·7	13·0
$V\ (\mathrm{CuS}) = \frac{95{\cdot}2}{4{\cdot}16} = 22{\cdot}9$	22·8	+0·1	14·8
$V\ (\mathrm{ZnS}) = \frac{97{\cdot}1}{4{\cdot}05} = 24{\cdot}0$	24·8	−0·8	14·9
$V\ (\mathrm{CdS}) = \frac{143{\cdot}7}{4{\cdot}8} = 29{\cdot}9$	28·6	+1·3	17·0
$V\ (\mathrm{HgS}) = \frac{231{\cdot}8}{8{\cdot}0} = 29{\cdot}0$	29·8	−0·8	14·9
$V\ (\mathrm{SnS}) = \frac{150{\cdot}8}{5{\cdot}0} = 30{\cdot}2$	32·1	−1·9	13·8
$V\ (\mathrm{PbS}) = \frac{238{\cdot}4}{7{\cdot}5} = 31{\cdot}8$	33·8	−2·0	13·7
		Mean	14·2

The agreement exhibited here is satisfactory, considering the difficulties surrounding the exact determination of the density. Consequently, no very great error would be made if the volumes of sulphur were calculated by subtracting from the volume of each sulphide the volume of the metal contained in it, thus :

$$V\ (\mathrm{ZnS}) - V\ (\mathrm{Zn}) = 24{\cdot}0 - 9{\cdot}1 = 14{\cdot}9 = V\ (\mathrm{S}).$$

In this manner the values under the heading V (S) in the above table have been obtained. The mean of these is 14·2 instead of 15·7. This difference appears to indicate that the combination is attended by a slight contraction.

The striking analogy exhibited by the elements sulphur and oxygen is sufficient to justify a calculation in a similar manner of the atomic volume of solid oxygen from the molecular volumes of the oxides. If this be done the following values are obtained, which agree fairly well with one another. In the following table in the first column are placed the stœchiometric values; under *d* in the second the density; under V in the third the volume of the oxide is given, and in the fourth under V (R) the volume of the metal; finally under V (O) the volume of oxygen, which is the difference between the two preceding sets of numbers.

		d	V	V (R)	V (O)
MnO	= 70·8	5·4	13·1	6·9	6·2
CoO	= 74·9	5·75	13·0	6·9	6·1
NiO	= 74·6	6·4	11·7	6·7	5·0
CuO	= 79·17	6·4	12·4	7·1	5·3
ZnO	= 81·1	5·7	14·3	9·1	5·2
CdO	= 127·7	6·95	18·3	12·9	5·4
SnO	= 134·8	6·3	21·4	16·4	5·0
HgO	= 215·8	11·3	19·1	14·1	5·0
PbO	= 222·4	9·4	23·7	18·1	5·6

Similar values may be obtained from the so-called sesquioxides R_2O_3.

		d	V	V (R_2)	V (O_3)	V (O)
Cr_2O_3	= 152·8	5·2	29·0	15·4	13·6	4·5
Mn_2O_3	= 157·5	4·8	32·7	13·8	18·9	6·3
Fe_2O_3	= 159·6	5·3	30·1	14·4	15·7	5·2
Co_2O_3	= 165·8	5·6	29·6	13·8	15·8	5·2
Ni_2O_3	= 165·1	4·9	33·7	13·4	20·3	6·8

These results show the space filled by the three atoms of oxygen to be nearly three times that occupied by one atom in the first series of oxides.

The values obtained for the atomic volume of oxygen are not always identical with those given in the above tables; thus, in the case of the oxides of the composition R_2O, *e.g.* Ag_2O, Cu_2O, Hg_2O, the space filled by the oxygen is much greater, whilst it is much smaller in the oxides RO_2; such as SnO_2 and SbO_2, *e.g.*

$$V\ (Cu_2O) - V\ (Cu_2) = 24{\cdot}9 - 14{\cdot}2 = 10{\cdot}7 = V\ (O)$$
$$V\ (SnO_2) - V\ (Sn) = 21{\cdot}7 - 16{\cdot}3 = 5{\cdot}4 = V\ (O_2)$$

In cuprous oxide the atom of oxygen would appear to occupy twice the space occupied by it in cupric oxide. In stannic oxide, on the other hand, the volume is only half as great. In the case of the compounds of the lighter metals still more remarkable relationships obtain. The production of the majority of these compounds is apparently attended by a considerable contraction; so much so indeed is this the case that the volume of the compound is smaller than that of the constituent metal; thus, for example:

$$V\ (Na_2O) = 22{\cdot}1,\ V\ (Na_2) = 47{\cdot}4$$
$$V\ (K_2O) = 35{\cdot}5,\ V\ (K_2) = 90{\cdot}4$$
$$V\ (MgO) = 12{\cdot}5,\ V\ (Mg) = 13{\cdot}9$$

It is needless to remark that in these and similar cases the method of interpretation employed in the case of the oxides cannot be used. Still some regularities amongst these compounds do become evident when a comparison is instituted between the volumes of analogous compounds of elements belonging to the same natural family or elements following one another in the periodic system. Still such relationships, despite the energy expended in their investigation, are at the present time but ill understood.

Of necessity the space filled by a solid body is not constant. Alterations in pressure, and more especially of temperature, affect this to a greater or less degree. When heat is applied to a solid body the volume increases. The expansion in the case of crystalline solids, save those crystallising in the regular system, is different in different directions; in fact, it appears probable that an expansion in one direction is accompanied by a contraction in another.

§ 65. **Fusion and Solidification.**—When heat is applied to a solid body, provided no chemical change is produced, then sooner or later the coherence of the particles is so far reduced that the solid melts; the individual particles are then able to move freely around one another, but still their coherence has not been completely overcome.

In many instances other changes of solidity precede the liquefaction, whilst in others, as soon as a definite temperature, the melting point, is attained the solids suddenly and completely liquefy. Others again soften or become pasty before melting, passing, in fact, through a state intermediate between the solid and the liquid. In this plastic condition particles can be welded together by pressure, as is the case with metals like iron and platinum. Some metals and some of the semi-metals, such as zinc, bismuth, and tellurium, before melting become brittle at a certain temperature, whilst at other temperatures they are malleable and ductile, and can then be either rolled into sheets or drawn into wire.

The change in the state of aggregation is associated with a greater or less absorption of heat. When the temperature of a solid is very much below its melting point, a definite amount of heat is required to produce a certain rise in temperature for each part by weight of the substance, and this is approximately the same for every degree of temperature. This amount of heat so required is styled 'the specific heat.' When the body begins to soften under the application of heat, the amount of heat required to produce a given rise in temperature increases more and more, until when the body melts the amount of heat absorbed is considerable, and is no longer perceptible as such, becoming, in fact, latent heat. The heat so absorbed serves in all probability to give an accelerated motion to the particles, and being thus converted into motion is no longer perceptible as heat. The fusion proceeds only in proportion as the heat is applied, and as this serves only for melting, the temperature remains stationary until the whole mass is fused. On the other hand, when a molten mass gives up the heat to surrounding objects its temperature is not necessarily lowered below the melting point, for the part solidifying will give out its latent heat of fusion. Nor is it until the whole has solidified that the temperature begins to sink. A molten body may, however, be frequently cooled below its melting point without solidifying. In this state of superfusion the particles are in a condition of unstable equilibrium, such that the slightest change suffices to bring about solidification. The solidification is more easily produced by contact with the minutest fraction of the solid itself. At the moment of solidification the temperature rises to that of the melting point but no further: this rise in temperature is produced by the liberation of the latent heat. This acceleration in the rate of motion of the particles corresponds to considerable increase in volume, which, as a rule, appears to take place suddenly on fusion or in part during the softening, this increase amounting in some cases to 12 or more per cent. of the volume of the solid. Yet in the case of some substances, especially water, cast iron, bismuth, and some of its compounds and alloys, and perhaps also in the case of other metals, contraction is known to attend the fusion: a fact which can perhaps be explained as arising from an altered arrangement of the atoms in the molecules. In water this contraction amounts to nearly 10 per cent. of the volume. The change in the state of aggregation produced by pressure depends upon whether fusion be attended by an expansion or contraction. A sufficiently great pressure produces that condition in which the material fills the smallest space. Ice can be liquefied by pressure, but most other solid substances can, by the application of high pressure, be retained in the solid state at temperatures much above their melting points.

§ 66. **Melting Points of the Elements.**—The temperatures at which different substances melt are specific and characteristic for each, and serve, therefore, as important aids for their identification. In § 36 it has already been mentioned that the fusibility of the elements is a periodic function of their atomic weights. This relationship, so far as it has been in any way ascertained, is exhibited in the following table. The melting points of many elements are still unknown, because the temperature at which they melt is either too high or too low to be accurately determined; in some other cases the rarity of the element or the difficulties surrounding its isolation have prevented the exact determination. In the following table the abbreviations used are: *a* = approximation, *b* = above, *c* = very low, *d* = very high, *e* = not melted, *rh* = red heat, *drh* = dull red heat, *brh* = bright red heat, *wh* = white heat.

MELTING POINTS OF THE ELEMENTS[1]

I	II	III	IV	V	VI	VII	VIII		
Li	Be	B	C	N	O	F			
180°	b r h	e	e	−214°	c	c			
Na	Mg	Al	Si	P	S	Cl			
96°	632°·6	654°·5	a 1500°	*44°*	114°	*−105°*			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
63°	d r h	?	e	e	d	w h	a 1600°	a 1500°	a 1450°
Cu	Zn	Ga	Ge	As	Se	Br			
1080°·5	418°·9	30°	a 900°	a 500°	a 680°	*−7°*			
Rb	Sr	Y	Zr	Nb	Mo	?	Ru	Rh	Pd
39°	d r h	?	a 1500°	d	d	?	a 2000°	a 1800°	a 1500°
Ag	Cd	In	Sn	Sb	Te	I			
960°·7	321°	*176°*	231°·9	629°·54	455°	114°			
Cs	Ba	La	Ce	Ta	W	?	Os	Ir	Pt
26°	d r h	a 800°	a 800°	d	d	?	a 2500°	1950°	1775°
Au	Hg	Tl	Pb	Bi					
1061°·7	*−39°*	249°	326°	268°					
			Th		U				
			d		b r h				

The elements are arranged in the horizontal lines in the order of their atomic weights. With these the melting point rises suddenly and falls suddenly; the minima of the melting points are printed in italics, the maxima in block print.

The periods of fusibility do not coincide with those of other physical properties—in fact, are less regular than these, but are nearly related, as has already been shown in § 36, to those of the atomic volumes.

It is remarkable that in every family the members of one group are difficult to fuse, whilst those of the other are easily fusible; *e.g.* lithium, sodium, potassium, rubidium, cæsium are easily fusible, whilst copper, silver, and gold melt at high temperatures, and similar relationships are found to exist in other families. In separate groups the melting point changes with the atomic weight, but not in the same manner. In some families the melting point falls with increase in atomic weight, thus:

Li 180°, Na 96°, K 63°, Rb 39°, Cs 26°,
Zn 419°, Cd 321°, Hg − 39°;

---

[1] The melting points for magnesium, aluminium, copper, zinc, silver, tin, antimony, and gold are taken from the paper of Heycock and Neville, *Chem. Soc. Journ.* lxvii. 160–199.

in others, again, it rises with increase in atomic weight; for example:— Ga 30°, In 176°, Tl 294°,
Cl – 105°, Br – 7°, I + 114°;
whilst in some families it rises at first to fall again, or falls first and then rises.

§ 67. **Melting Points of Compounds.**—In the melting points of compounds we have similar differences to those exhibited by the elements. By the introduction into a compound of certain elements the fusibility is in some cases raised, in other cases lowered. The oxides of metals, *e.g.* melt at much higher temperatures than the metals themselves; the majority of the oxides of the non-metals melt more easily than the elements; in one and the same group of elements these changes, as a rule, are found to be of the same character, but even in this case also there are exceptions. Whilst, for example, the infusible element carbon yields an oxide (CO_2) which melts at –60°, the corresponding oxide (SiO_2) of the infusible silicon has almost as high a melting point as the element itself. Fluorides, chlorides, bromides, iodides, melt, as a rule, much more easily than the oxides, and usually the iodide of an element is more easily fusible than the bromide, and this than the chloride, whilst the fluoride has the highest melting point. Thus, for example, the melting points of halogen compounds of the alkali metals are, according to Carnelley, as follows:[1]

—	Li	Na	K	Rb	Cs
F	801°	902°	789°	753°	?
Cl	598°	722° (^{1}815°·4)	734° (800°)	710°	631°
Br	547°	708° (757°·7)	699° (722°)	683°	?
I	466°	628° (661°·4)	634° (684°·7	642° (641°·5)	? (621°)

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[1] The numbers in brackets in this table are taken from the results of Victor Meyer, W. Riddle, and Th. Lamb (*Ber. der deut. chem. Ges.*, 27, 3,129). Somewhat similar results have been obtained by McCrae (*Wiedem. Annal.* 55 45).

The melting point falls, therefore, with increased atomic weight of the halogen, and similar relationships are to be found in other families of the elements.

Many similar regularities are to be found amongst organic compounds; still our knowledge of the general laws in this province is much less extensive than might be imagined from the thousands of melting-point determinations which have been made.

It is, however, to be observed that in many cases the repeated introduction of a given atom or a group of atoms in an organic compound is accompanied by alternate raising and lowering of the melting point. This, as was first shown by Baeyer, is the case in the normal primary fatty acids of the general formula $C_nH_{2n}O_2$. In these compounds the atom linkage is represented as follows:

$$HO—CO—CH_2— \ . \ . \ . \ CH_2—CH_2—H$$

in accordance with which the several members of the series differ from one another only in the number of CH_2 groups introduced between the carboxyl group, COOH, and hydrogen. The relationships are shown in the following table:

Name	Formula	Melting Point	
Formic Acid . . .	CH_2O_2		+ 8°·4
Acetic Acid . . .	$C_2H_4O_2$	+ 17°	
Propionic Acid . . .	$C_3H_6O_2$		− 24°
Butyric Acid . . .	$C_4H_8O_2$	+ 1°	
Valerianic Acid . . .	$C_5H_{10}O_2$		below − 16°
Caproic Acid . . .	$C_6H_{12}O_2$	− 2°	
Heptylic Acid . . .	$C_7H_{14}O_2$		− 10°·5
Caprylic Acid . . .	$C_8H_{16}O_2$	+ 16°·5	
Pelargonic Acid . . .	$C_9H_{18}O_2$		+ 12°·5
Capric Acid . . .	$C_{10}H_{20}O_2$	+ 30°	
Undecylic Acid . . .	$C_{11}H_{22}O_2$		+ 28°·5
Lauric Acid . . .	$C_{12}H_{24}O_2$	+ 43°·6	
Tridecylic Acid . . .	$C_{13}H_{26}O_2$		+ 40°·5
Myristic Acid . . .	$C_{14}H_{28}O_2$	+ 58°·8	
Quindecylic Acid . .	$C_{15}H_{30}O_2$		+ 51°
Palmitic Acid . . .	$C_{16}H_{32}O_2$	+ 62°	
Margaric Acid . . .	$C_{17}H_{34}O_2$		+ 60°
Stearic Acid . . .	$C_{18}H_{36}O_2$	+ 69°	
—	$C_{19}H_{38}O_2$		?
Arachic Acid . . .	$C_{20}H_{40}O_2$	+ 75°	
Medullinic Acid . . .	$C_{21}H_{42}O_2$		72°·5
Behenic Acid . . .	$C_{22}H_{44}O_2$	+ 73°	

From the above it is seen that the first introduction of the group CH_2 between the carboxyl and hydrogen raises the melting point, whereas the introduction of the second group lowers the melting point; consequently those members in this series of acids which contain an uneven number of carbon atoms melt at a lower temperature than either of their neighbours containing an even number of carbon atoms. As the molecular weight increases, this difference gradually disappears. The melting point of the dibasic acids of the formula,

$$C_nH_{2n-2}O_4 = HO—CO—(CH_2)_m\,CO—OH,$$

consisting of oxalic, malonic, and succinic acids, &c., exhibit similar relationships.

The melting point of many hydro-carbons, *e.g.* of benzene, as shown by Jungfleisch, is alternately raised and lowered by the replacement of the hydrogen by chlorine.

—	Melting Points	
C_6H_6	+ 3°	
C_6H_5Cl		− 40°
$C_6H_4Cl_2$	+ 53°	
$C_6H_3Cl_3$		+ 17°
$C_6H_2Cl_4$	+ 139°	
C_6HCl_5		+ 86°
C_6Cl_6	+ 228°	

Still, it is only when the chief products of the action of chlorine upon benzene are compared with one another that such regularities are observed. In addition to these, several isomeric compounds are formed, but in much smaller quantities, and these again have different melting points. In fact, it is found that the melting point of a compound is influenced by the positions which the chlorine atoms occupy relatively to one another.

As a general rule, it may be stated that of the three isomeric di-substitution products[1] which may be obtained by replacing two atoms of hydrogen in benzene by two other atoms or radicals, the para- compound has a melting point much higher than the ortho- and the meta-. Which of the latter has the higher melting point depends upon the nature of the atom or radical replacing the hydrogen. If one of these is the carboxyl group, COOH, then the meta- compound has a higher melting point than the ortho-, otherwise the ortho- compound will melt at the higher temperature. Still these rules are not without exceptions; in the presence of the nitro- group, NO_2, it sometimes happens that the ortho- is more easily fusible than the meta-, and in some cases the reverse obtains. The following examples will serve to illustrate these points:

---

[1] Cf. § 51.

—	—	—	Para-	Meta-	Ortho-
C_6H_4	Cl	Cl	53°	under −15°	below −14°
„	Br	Br	89°	−28°	−1°
„	I	I	127°	40°	94°
„	Cl	I	56°	?	liquid
„	Cl	Br	67°	liquid	?
„	Br	I	92°	liquid	liquid
„	OH	OH	172°	99°	112°
„	NH_2	NH_2	140°	63°	99°
„	„	Br	64°	18°	31°
„	„	I	60°	25°	?
„	CH_3	CH_3	15°	−54°	−28°
„	COOH	OH	210°	200°	156°
„	„	OCH_3	175°	106°	99°
„	„	Cl	234°	152°	137°
„	„	Br	250°	155°	148°
„	„	I	267°	185°	159°
„	„	NH_2	187°	174°	144°
„	NO_2	NO_2	171°	90°	118°
„	„	I	171°	36°	49°
„	„	Cl	83°	44°	32°
„	„	Br	126°	56°	42°
„	„	NH_2	146°	110°	71°

When a third atom of hydrogen in benzene is replaced, then the melting point is altered still more; as a rule, the melting point of a para- compound is lowered, and indeed often very considerably; whilst those of the other isomeric di-substitution products are raised. Still, even in this case the change in the melting point is determined, not only by the nature of the replacing radical, but also by their relative positions. In the most symmetrical arrangements of these several groups in the position 1 . 3 . 5 (*vide* § 54) the melting point is found to attain the maximum.

§ 68. **Melting Points of Mixtures.**—Heterogeneous solid bodies melt either in such a way that only one portion is liquefied, whilst the other remains solid or all the several constituents become liquid simultaneously. In the last case the fusion always takes place at a fixed temperature, which may be below the melting point of the less easily fusible constituent, and is frequently found to be lower than the melting point of the most easily fusible component. In this we have an explanation of the observations so frequently made in laboratory practice that even very small impurities suffice to effect a considerable reduction in the melting point of a substance. Such a mixture can frequently be distinguished from a pure homogeneous substance by the fact that the temperature does not remain stationary during the fusion. As a rule, the constituent with a lower melting point melts first, and with it only a part of the higher melting constituent, the remainder of the latter continuing in the solid state, and not melting until a higher temperature has been reached. If one were to separate the liquid portion from the solid before this had occurred, then each portion when separately examined would be found to possess a higher melting point, because it contains a smaller portion of impurity. An excellent method for the purification of solids is based upon this difference.

§ 69. **Homogeneous Liquids, Cohesion, Capillarity, Friction.** As has already been pointed out in § 60, the liquid state of aggregation is distinguished by the fact that the particles, although held together, can move easily over one another. In consequence of this, liquids under the influence of the force of gravity assume the form of the vessel containing them; whilst the surface assumes a direction perpendicular to the line of the action of gravity, provided that other forces—*e.g.* the centrifugal force—do not tend to change this position. The space occupied by a liquid can only be reduced to a very small extent by great pressure; liquids are therefore only slightly compressible fluids.

The mobility of the particles is very different in different liquids. On the one hand we have liquids possessing a so-called syrupy consistence; on the other hand, those possessing a mobility approached very nearly to that characteristic of gases. The resistance which they offer to movement is what is usually styled the internal friction or the viscosity of the liquids. This property may be determined from the velocity with which the liquid flows through a narrow tube (transpiration according to Graham), or by the retardation, which a body rotating round its axis experiences when set in motion in such liquids. The friction is dependent upon the nature and composition of the liquid; still, too little is known of the connection between these properties to allow of any general statement being made.

Nor is our knowledge of the manner in which the particles of a liquid are held together in a much more advanced state, the cohesion of liquids, which is especially exhibited in the phenomena of capillarity, *i.e.* the manner in which liquids rise in very narrow tubes, the walls of which are moistened by them, and is likewise shown in the formation of drops. The weight or volume of the liquid raised by capillarity is dependent upon the chemical nature and composition of the liquid; still, of this inter-dependence so little is known that it would not be advisable to discuss it further.

§ 70. **Density of Liquids.**—The subject of the density or the specific gravity of liquids, *i.e.* the weight of a unit volume, is one which has been exhaustively investigated. Usually, however, it is not the density, but rather its reciprocal, the so-called specific volume—that is, the volume of the unit of weight—which is dealt with in these investigations. The product of these values into the atomic weights of elements and into the molecular weights of compounds gives the atomic and molecular volumes. Relationships have been recognised amongst these values similar to those found to obtain in the case of solids (*vide* § 64). As the majority of elements are only to be obtained in the liquid state, at either inconveniently low or high temperatures, their atomic volumes in the liquid state have been but little studied.

Inasmuch as for an equal rise in temperature liquids expand much more easily than solids, it is important in the case of liquids that comparisons should be instituted at corresponding temperatures. Hermann Kopp proposed that this comparison in the case of liquids should be made at a temperature at which their vapour pressures are the same, viz.

at the boiling point under the same pressure. The pressure usually taken as normal is the mean atmospheric pressure, viz. 760 millimetres, although in the light of the more recent investigations it would appear more desirable to choose a much smaller pressure. But even the molecular volumes of compounds compared at their boiling points under the atmospheric pressure, more especially those of organic compounds, exhibit numerous relationships, which, although they cannot be regarded as fixed natural laws, may at any rate be taken to represent approximations to such laws.

The fundamental law of atomic volumes is that every atom in a compound at its boiling point occupies a given space which is chiefly determined by its nature, and only to a limited extent by the manner in which it is combined; so that the volumes occupied by the molecular weights of different compounds may be taken to be represented by the sum of the volumes of all the atoms contained in them.

Thus if V be this volume, then in the case of alcohol we have the following:

$$V(C_2H_6O) = 2V(C) + 6V(H) + 1V(O);$$

and similarly in other compounds.

The unit of volume in this case is the space which the unit weight of water at its maximum density occupies, and the unit of weight the weight of an atom of hydrogen. The value of this latter unit is unknown, but that does not signify, as in this case it is, as in all determinations of density, only a question of relative values. In fact, the same values for the molecular volumes are obtained if, instead of an atom, one gramme of hydrogen is taken as the unit of weight and one cubic centimetre as the unit of volume.

Expressed in these terms, according to Kopp's determinations, the volumes of the atoms of the following elements in their compounds at their boiling points would be approximately the following:

$$V(H) = 5{\cdot}5,\ V(C) = 11,\ V(O) = 7{\cdot}8.$$

Accordingly in the case of alcohol, already cited, the following value should be obtained:

$$2V(C) + 6V(H) + 1V(O) = 22+33+7{\cdot}8 = 62{\cdot}8;$$

whilst the actual determination at the boiling point 78° C. shows the molecular volume of alcohol to be 62·2.

From Kopp's law it follows, then, that a fixed difference in the composition must always be associated with a similar difference in the molecular volumes; thus, for example, the difference CH_2 in a homologous series of compounds must give rise to a difference in volume. This difference in volume for every addition of CH_2 has been found to be 22; and similar differences will be found in other cases. The agreement between the calculated and the observed values is, however, only approximate; thus, *e.g.*, for the first five members of the series of alcohols $C_nH_{2n+2}O$ the following values have been obtained:

n	V calculated	Difference	V observed	Difference
1	40·8	22	42·7	19·5
2	62·8	22	62·2	19·1
3	84·8	22	81·3	20·3
4	106·8	22	101·6	21·1
5	128·8		122·7	

The deviations from this fundamental rule may in many cases be attributed to differences in the mode of linkage of the atoms. Thus, for instance, two polyvalent atoms occupy less space when united to each other by single affinities than when two or more combining units are used for their mutual combination. Thus the following relations are found to hold:

$$V(-O-C\equiv) < V(O=C=)$$
$$V(-S-C\equiv) < V(S=C=)$$
$$V(=N-C\equiv) \quad V(N\equiv C-)$$
$$V(\equiv C-C\equiv) < V(=C=C=) \text{ \&c.}$$

This and similar relationships have been frequently used in the investigation of atomic linkage; still, it must be remembered that conclusions drawn from such observations are always more or less uncertain, as there are many deviations from this rule which cannot be explained as due to variations in the mode of union of the atoms. In the meantime investigations of this kind are being steadily carried on. It has, for instance, been shown that when an atom of chlorine or of bromine replaces an atom of hydrogen in organic compounds, the space occupied by the atom of the halogen element is dependent upon the position it occupies, being greater when attached to one atom than when combined with another. In the case of benzene substitution products, the radicals replacing hydrogen in this hydrocarbon have a greater volume when they occupy the para- position than in the meta-, and in the meta- position a greater volume than in the ortho- position. All such results are of great importance as contributing to our knowledge of the properties of matter.

§ 71. **Expansion by Heat.**—The volume of a liquid varies with the temperature, and as a rule the alterations produced by given changes of temperature are greater in the case of liquids than for solids. Usually the volume increases with rise in temperature, and this expansion becomes greater and greater as the temperature rises. It is only in the neighbourhood of the solidifying point that some liquids, notably water (§ 65), are found to contract in volume as their temperature is raised.

Van der Waals has deduced theoretically the law which controls the expansion of liquids by heat, and has demonstrated the truth of the law by a comparison of the deductions made from it with the results of observation. For such comparisons a knowledge of the critical temperature (*v.* § 86) of a liquid is required, which still remains unknown for the majority of those liquids the co-efficients of expansion of which have already been determined.

The expansion of a liquid is attended by a considerable absorption of heat, which with one and the same substance is, for an equal interval of temperature, greater when in the liquid state than when in the solid condition. The heat capacity or the specific heat of a given substance is greater in the liquid state than in the solid, often twice as great, and is even greater in the liquid than in the gaseous state.

By multiplying the specific heat into the molecular weight the so-called molecular heat is obtained, which in the case of homologous organic compounds changes with tolerable regularity.

§ 72. **Refraction of Light by Liquids.**—The refraction of light by liquids has been very completely investigated. It has been found to be dependent upon the nature and the amount of the elements contained in the liquids, as also upon the manner of their union with one another. This interdependence has been specially studied and demonstrated for the compounds of carbon, the so-called organic compounds, and for many others also.

If n be taken to represent the refractive index of a liquid, and d its density, then it can be shown theoretically that the quotient[1]

$$\frac{n^2-1}{(n^2+2)d},$$

which is known as the specific refractive power, is practically unaffected by temperature; a conclusion which has been substantiated by actual observation. With the aid of this expression one may, as has been shown by Gladstone and Dale, by Landolt and his pupils, represent the specific refractive power of a liquid as made up of the sum of the refractive powers of its constituents. If the weight P of the liquid contains p_1, p_2, p_3, &c. weights of the constituents, then the following relation will obtain, in which N and D represent the refractive index and density of the liquid, and n_1, n_2, n_3, d_1, d_2, and d_3 are the refractive indices and densities respectively of the constituents:

$$\frac{N^2-1}{(N^2+2)D}\cdot P = \frac{n_1^2-1}{(n_1^2+2)d_1}\cdot p_1 + \frac{n_2^2-1}{(n_2^2+2)d_2}\cdot p_2 + \frac{n_3^2-1}{(n_3^2+2)d_3}\cdot p_3 + \ldots$$

Landolt's investigations have shown that this expression applies equally to mechanical mixtures and to chemical compounds.

If, therefore, P be the molecular weight, M, made up of x atoms of A_1, of y atoms of A_2, &c. then, since

$$P = M = xA_1 + yA_2 + zA_3 + \ldots$$

---

[1] Until recently the simpler expression $\frac{n-1}{d}$ was employed to represent the specific refractive index, instead of the expression deduced by H. A. Lorentz and L. Lorenz. The simpler expression, which was arrived at empirically, explains satisfactorily the majority of observed facts, but is not, according to Brühl, so satisfactory in some cases.

it follows that

$$\frac{N^2-1}{(N^2+2)D} \cdot M = x \frac{n_1^2-1}{(n_1^2+2)d_1} \cdot A_1 + y \frac{n_2^2-1}{(n_2^2+2d)_2} \cdot A_2$$

$$+ z \frac{n_3^2-1}{(n_3^2+2)d_3} \cdot A_3 + \ldots$$

Or that the molecular refractive power or the molecular refraction of a compound is the sum of the refraction equivalents of its constituents. The refraction equivalent of the elements, which is here represented by the expression

$$\frac{n^2-1}{(n^2+2)d} \cdot A,$$

may, in the cases in which these values are known, be calculated from the refractive index n, the density d, and the atomic weight A. It is, however, more convenient to deduce these values from the observed molecular refraction of compounds, which differ in composition by a definite number of atoms of one or other of the elements. Calculations of this kind, based upon data supplied by a very extensive series of observations, have been carried out in numerous instances.

Since light of different colours is refracted differently, the index of refraction, n, must vary with the colour; consequently observations made with light of different colours yield different refraction equivalents for one and the same substance. Inasmuch as up to the present no formula has been discovered which enables one to eliminate satisfactorily this influence of colour, the index of refraction is determined for light of a fixed colour,[1] for instance, that corresponding to Fraunhofer's line C in the sun's spectrum is frequently used for this purpose, and this is identical with the red line in the hydrogen spark spectrum. For this coloured light Landolt found the following to represent the molecular refractions (Mrf) of the compounds in the two following tables, each of which consists of a series of compounds differing from each other by constant difference (CH_2):

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[1] Recently Landolt and Jahn have shown this may be also done with the long electric waves.

Name	Formula	Difference	Mrf	Difference
Water	H_2O		3·69	
Wood Spirit	CH_4O	CH_2	8·16	4·47
Ethyl Alcohol	C_2H_6O	CH_2	12·71	4·55
Propyl „	C_3H_8O	CH_2	17·28	4·57
Butyl „	$C_4H_{10}O$	CH_2	21·96	4·68
Amyl „	$C_5H_{12}O$	CH_2	26·59	4·63
				Mean 4·58

Name	Formula	Difference	Mrf	Difference
Formic Acid	CH_2O_2		8·52	
Acetic Acid	$C_2H_4O_2$	CH_2	12·93	4·41
Propionic Acid	$C_3H_6O_2$	CH_2	17·42	4·49
Butyric Acid	$C_4H_8O_2$	CH_2	22·01	4·59
Valerianic Acid	$C_5H_{10}O_2$	CH_2	26·72	4·71
Caproic Acid	$C_6H_{12}O_2$	CH_2	31·22	4·50
Œnanthic Acid	$C_7H_{14}O_2$	CH_2	35·85	4·63
				Mean 4·56

A difference in composition of one atom of carbon and two atoms of hydrogen is seen from the above to produce a difference of 4·57 in the molecular refraction. Similarly, the effect on the molecular refraction may be determined for other differences in composition, and from such results the refraction equivalents of individual elements may be calculated. The following represent the refraction equivalents of some of the commoner elements, for the Fraunhofer line C, or the line *a* in the hydrogen spectrum :

		Refraction Equivalent
Carbon	C	2·48
Hydrogen	H	1·04
Oxygen	O	1·58
Chlorine	Cl	6·02
Bromine	Br	8·95
Iodine	I	3·99
Nitrogen	N	3·02

By the aid of such numbers the molecular refraction of a compound like ethyl alcohol, for instance, may be calculated, thus :

$$C_2H_6O = 2 \times 2{\cdot}48 + 6 \times 1{\cdot}04 + 1 \times 1{\cdot}58 = 12{\cdot}78.$$

The observed refraction for ethyl alcohol is 12·71. Similarly, the molecular refractions of other compounds may be calculated.

§ 73. **Influence of Atom-linkage on Refraction.**—Such agreement between the observed and calculated results does not obtain in all cases; as, for instance, in the following we have

Aldehyde, C_2H_4O, Mrf $= 2 \times 2{\cdot}48 + 4 \times 1{\cdot}04 + 1 \times 1{\cdot}58$
$= 10{\cdot}70$ (observed 11·50).

Acetic acid, $C_2H_4O_2$, Mrf $= 2 \times 2{\cdot}48 + 4 \times 1{\cdot}04 + 2 \times 1{\cdot}58$
$= 12{\cdot}28$ (observed 12·93).

Valerianic acid, $C_5H_{10}O_2$, Mrf $= 5 \times 2{\cdot}48 + 10 \times 1{\cdot}04 + 2 \times 1{\cdot}58$
$= 25{\cdot}96$ (observed 26·72.)

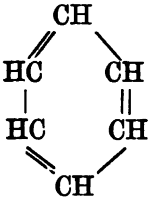
In each of these three instances the experimental values are greater than the calculated, and the difference is very nearly the same in each case, thus:

$$11{\cdot}50 - 10{\cdot}7 = 0{\cdot}8;\ 12{\cdot}93 - 12{\cdot}28 = 0{\cdot}65;$$
$$26{\cdot}72 - 25{\cdot}96 = 0{\cdot}76.$$

The molecular refractions of acids, aldehydes, ketones, ethereal salts, and those compounds derived from them are found to be greater than the calculated values, and in these compounds it is assumed for several reasons that they contain an atom of oxygen united to an atom of carbon by both its affinities. If it be assumed that the refraction equivalent of oxygen when so combined is 2·34—that is, 0·76 greater than its refraction equivalent in the alcohols and other similar compounds—then we obtain calculated results exhibiting a satisfactory agreement with the results of observation.

Investigations undertaken at the suggestion of Landolt by J. Brühl have shown that the so-called unsaturated carbon compounds, viz. such compounds as combine directly with chlorine, bromine, or even hydrogen, possess a molecular refraction greater than those obtained by calculation. From the numerous cases investigated it is found that a satisfactory agreement between the calculated and observed results is obtained when to the calculated molecular refraction 1·79 is added for every pair of carbon atoms united by double combining units, and 1·97 must be added for every pair of carbon atoms united by three combining units.

After these rules had been established chemists sought by their aid to determine the mode of atomic linkage in various organic compounds, and more especially to fix the number of the groups of carbon atoms united by two or three combining units. It has thus been shown to be extremely probable that in benzene, toluene, and analogous hydrocarbons there are three pairs of carbon atoms united by two combining units, as is required to satisfy Kekulé's constitutional formula (§ 51):



The molecular refraction of benzene and its derivatives has been found to be about five units greater than the sum, S, of the refraction equivalents of the elements contained in them, as will be seen from the following examples:

—	—	Molecular Refraction	Sum S	Difference
Benzene . .	C_6H_6	25·93	21·12	4·81 = 3 × 1·60
Toluene . .	C_7H_8	30·79	25·68	·511 = 3 × 1·70
Mesitylene . .	C_9H_{12}	40·33	34·80	5·53 = 3 × 1·84
Phenol . . .	C_6H_6O	27·85	22·70	5·05 = 3 × 1·68
Benzyl Alcohol .	C_7H_8O	32·23	27·26	4·97 = 3 × 1·66

This and similar applications have combined to make the molecular refraction a very important aid in the investigation of the mode of linkage of the atoms in different compounds.

§ 74. **Interaction of Liquids with other Substances. Gelatinous Hydration.**—If a liquid be brought into contact with another liquid or with a solid body upon which it has no chemical action, the change resulting from this contact will depend upon the material composition of both, and determined by this, mixing, or dissolution, or mere contact will result. Liquids which do not mix with one another will arrange themselves in accordance with their specific gravities, liquids of equal densities forming spherical drops in the mass of the other.

If one of the immiscible substances is a liquid and the other a solid, then one of two sets of phenomena will be produced; either the liquid wets or moistens the solid, and in that case we have the phenomenon of capillary attraction and the liquid is raised in the solid, or the liquid does not wet the solid, then at the point of contact a depression of the liquid surface is produced. Thus, as is well known, water, spirits of wine, oils, and many other liquids rise on the surfaces of glass, whilst mercury is depressed by glass, just as the surface of water is depressed by contact with fat. In such cases the nature of the solid body is of importance only so far as it determines whether it is moistened or not by the liquid; in other respects the capillary ascent or depression is dependent upon the nature of the liquid alone.

There is a class of solids which possess the remarkable property of absorbing liquids, by which they are moistened, without dissolving in these same liquids.

This absorption of liquids is usually accompanied by a considerable increase in the volume of the solid, and is described as 'gelatinous hydration' or 'imbibition.' Cellulose, starch, glue, coagulated albumen, and many other substances swell up when brought into contact with water, and caoutchouc behaves similarly when moistened by ether. To those substances which exhibit this phenomenon is ascribed a large molecular weight and an atom-linkage of such a character that the atoms form a species of network into the spaces which the smaller molecules of liquids are able to penetrate without destroying the network. It is worthy of remark that frequently phenomena such as diffusion (§ 80) can proceed in the interior of the absorbed liquid as well as in that portion which has not been so taken up. This power of absorption is very different for different substances; whilst in many cases the volume of a solid is considerably increased during the process of imbibition, in some cases the increase is scarcely perceptible. We are acquainted with all the intermediate stages exhibited by this class of bodies, and by substances such as burnt clay, hydrophane, &c. which, possessing a visibly porous structure, take up liquids into their pores, which serve simply to wet the interior of the pores.

§ 75. **Heterogeneous Mixtures of Liquids. Solutions.**—Many substances are able to form fluid mixtures with other bodies. Such mixtures are usually styled 'solutions' or 'dissolutions,' one constituent being distinguished as the solvent, the other as the dissolved substance. Such distinctions are entirely arbitrary and have no scientific import.

Fluid mixtures may be produced in the following ways:

(1) By solid bodies alone.
(2) By solids and liquids.
(3) By liquids alone.
(4) By liquids and gaseous bodies.
(5) By gases alone.
(6) By gases and solids.

The states of aggregation of the constituents of such liquids only affect the nature and properties of the mixture so far as the constituents assume these conditions or states on separating out from the mixture. So long as they exist in the mixture, they must be regarded as liquids.

The quantities of the constituents in such a fluid mixture or solution are either quite unlimited, the mixing taking place indefinitely in any proportions, or the proportions are so limited that the admixture takes place only within certain limits, beyond which it is not possible to pass.

The first of these cases is represented by liquids such as water and alcohol, ethyl alcohol and methyl alcohol, or water and glycerol, which mix with one another in every proportion.

In those cases in which such mixing or solution takes place only within certain limits the maximum amount of one of the substances which is taken up by a definite proportion of the other, say 100 or 1,000 parts by weight of this substance, is styled the 'solubility' of the first in the second. When both substances are liquids, then the proportion of one of these may be raised from zero to a certain fixed limit, but this latter cannot be exceeded. If more than this amount be added, then it remains in the liquid state and separates from the rest; it can, on its part, however, take up some of the other constituent. According to Schuncke, water at 20° C. can take up 0·075 of its weight of ether, whilst this latter may take up as much as 0·027 of its weight of water. Mixtures of ether and water, therefore, can only be obtained containing from 0 to 7 or from 97 to 100 parts by weight of ether in 100 parts of the mixture. Consequently at 20° C. mixtures of ether and water can only be produced containing less than 7 or more than 97 parts by weight of ether.

When one of the bodies is a liquid and the other a solid, then, whilst the proportion of the former may be raised indefinitely, that of the latter is fixed within a certain maximum limit, any excess above this amount remaining undissolved and generally in the solid state, though in some cases, as with phenol and water, in a fluid condition. Solutions which are incapable of dissolving any more of the solid are said to be 'saturated.'

When both constituents are solids, but the mixture formed by them a liquid, then, as in the case of salt and ice, there is for both of the constituents of the solution an upper and lower limit; neither of these limits must be exceeded if the mixture is to remain liquid.

§ 76. **Effect of Heat on Solubility.**—The dissolution and also the solubility of different bodies are considerably affected by heat, the effects being analogous to those produced on simple unmixed substances. With such simple bodies an increase of volume is associated with an absorption of heat: a reduction in volume, with a loss of heat; so also, as a rule, in the admixture of liquids, a contraction is attended by an evolution of heat, which may be, and often is, considerable.

The changes in aggregation associated with dissolution are also frequently accompanied by considerable thermal disturbances.

Just as when a solid body is melted, heat is rendered latent, so also there is a reduction in temperature attending the dissolution of a solid. The reduction in temperature is especially great when both the bodies passing into solution are solids. Thus, by mixing salt and ice in suitable proportions, the temperature of the mass can be lowered by

20° C. The heat so disappearing or becoming 'latent' is used in the conversion of the solid into the liquid state. Many substances first combine chemically with a portion of the solvent, and the compound so produced is then dissolved. Thus, for instance, anhydrous calcium chloride when brought into contact with water combines with the latter with production of heat to form the crystallisable compound $CaCl_2 6H_2O$, which dissolves in water with a considerable absorption of heat. For the production of cold, therefore, hydrated, and not anhydrous, substances are best adapted.

The limits of solubility are altered by changes of temperature, and in the majority of cases a rise in temperature increases the solubility. Still there are exceptions to this rule, and more especially in the case of liquids. Thus, for example, ether is less soluble in warm water than in cold, and consequently a cold saturated solution of ether in water becomes turbid when heated, owing to the separation of ether from the water.

According to Alexejeff, in the case of aniline and water the mutual solubility of each is increased by rise in temperature. At low temperatures solutions can only be obtained containing but little water and very little aniline. As the temperature rises their solubility in each other increases, so that at 167° C. these substances may be mixed with each other in any proportion.

A reduction in the solubility with rise in temperature has been observed only in the case of a few solids, and in these cases the substances undergo a change in their chemical composition; as, for instance, they may lose their water of crystallisation or some other similar change may take place. The degree of solubility is, as a rule, very considerably increased by a rise in temperature; in some cases, however, the alteration is but slight.

In consequence of this marked increase of solubility, a hot saturated solution when cooled must deposit a portion of the dissolved substance. This as a matter of fact does take place, accompanied by an evolution of the latent heat, which had disappeared in the dissolution. In the separation of solids from their hot saturated solutions we have an excellent means for purifying many substances; for, when the solution is saturated with one substance and not with the impurity, then the first of these alone separates out, unless there are special conditions which may cause the deposition of the impurity.

§ 77. **Crystallisation. Supersaturation.**—A hot saturated solution may, when suitably protected from external influences, retain on cooling an excess of the dissolved substance, just as a fused substance may, if carefully cooled below its melting point, still be maintained in the liquid state (§ 65). Such solutions are described as 'supersaturated,' just as simple substances are said to be 'superfused.' These states of supersaturation and of superfusion are no doubt determined, more especially of crystals, by the circumstance that a certain impetus is needed for the formation of solid aggregates, without which they are not formed. Mechanical disturbance, such as shaking or contact with a solid, may bring about solidification; a particle of a crystal of the solid itself or of an isomorphous body is most effective in causing the separation of a solid from a supersaturated solution, or the solidification of a superfused liquid. The crystal acts on the particles surrounding it, in such a manner that by arranging themselves around it, and then by becoming attached to the crystal, they cause it to grow. It is not uncommon to obtain solutions which can only be induced to crystallise by making use of these facts. Crystals when introduced into supersaturated solutions, as a rule, only cause the separation of substances of the same composition as themselves, so that the solution may remain supersaturated for another solid. This does not obtain when the substances in solution are isomorphous, for then the introduction into the solution of a crystal of either of them would cause the crystallisation of both of the isomorphous bodies, whatever the proportion in which they exist in the solution.[1] Consequently isomorphous bodies cannot be separated from one another by recrystallisation.

When the temperature of a solution falls below the freezing or melting point of the liquid constituent, *e.g.* of water, then we have a phenomenon similar to that which in § 75 was described as characteristic for a fluid mixture formed by solids only. There is now, therefore, a lower limit of solubility as well as an upper limit, so that neither of the constituents must be present in less than certain proportions, if the other is not to solidify.

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[1] Ostwald (*Zeitschr. f. phys. Chem.* 22, 289–330) has recently attempted to determine the smallest amount of a crystal required to start crystallisation in supersaturated solutions and in superfused liquids.

The further the temperature sinks, so much the nearer do these limits come together and finally coincide; consequently at the lowest temperature only one liquid mixture can exist. A concentrated aqueous solution of common salt will deposit salt on cooling; whilst ice separates from a dilute solution cooled below the freezing point. The further the temperature sinks the more nearly do both solutions approach one another in composition, until at −22° C. they have the same composition and contain one part of salt to three parts of water.

Further cooling would effect a solidification of the whole; a liquid mixture of salt and ice cannot, therefore, exist below this temperature.

§ 78. **Relations between the Freezing Points of Solutions and the Molecular Weights of their Constituents.**—Rüdorff and de Coppet have found that the freezing point of a not too concentrated solution of salt sinks in proportion to the amount of salt present. One part of common salt dissolved in 100 parts of water reduces the freezing point of water from zero to $-0^\circ{\cdot}6$ C., two parts reduce it to $-1^\circ{\cdot}2$ C., four parts to $-2^\circ{\cdot}4$ C., six parts to $-3^\circ{\cdot}6$ C., and so on; for every further additional part of salt a reduction of $0^\circ{\cdot}6$ C. is produced till the proportion of salt in the solution amounts to 14 in 100, when the solution freezes at $-8^\circ{\cdot}4$ C.

At first sight it would appear that below this temperature the relation between the proportion of salt and the reduction in the freezing point ceases. Further investigation has, however, shown that this relationship still exists even at this temperature, but no longer holds for anhydrous salt, but for the compound $NaCl + 2H_2O$, which is the compound crystallising from water at this lower temperature.

We may therefore conclude that below the limit between −8° and −9° C. the solution contains this compound, and not the anhydrous salt.

In other cases, even with salts crystallising with water at higher temperatures, the reduction of the freezing point below zero is found to be proportional to the amount of the hydrated salt present in the solution. For instance, for sodium iodide the reduction is proportional to the compound $NaI + 4H_2O$ in 100 parts of water. This reduction of freezing point is therefore an excellent means of deciding the question as to whether a given salt, when dissolved in water, loses or retains its water of crystallisation. All that is necessary is simply to determine the freezing point of solutions of different concentration, and in this way ascertain whether the lowering of the freezing point is in proportion to the amount of the hydrated or of the anhydrous salt in solution.

The results obtained by this method of investigation have in many cases been confirmed by other observations, more especially of the colour of the solution, when the hydrated salt differs in colour from the anhydrous salt. For instance, anhydrous copper sulphate, $CuSO_4$, is colourless, whilst the hydrated blue vitriol, $CuSO_4 + 5H_2O$, is blue, so also is the solution; therefore the solution must contain the hydrated and not the anhydrous salt. This conclusion is confirmed by the results of the determination of the freezing point of its solutions.

If the reduction in the freezing point, instead of being calculated for one part by weight, is calculated for the stœchiometric amount represented by its formula, viz. the quantity Q, then substances of analogous composition yield very nearly equal values. In the following table under Q are given the weights of each of the compounds dissolved in 1,000 parts of water, the freezing points are given under E Q, and under E the depression in the freezing point produced by one part by weight of the salt:

—	Q	E	E Q
Sodium Chloride	$NaCl = 58{\cdot}4$	0°·0600	−3°·50
Potassium Chloride	$KCl = 74{\cdot}4$	0°·0446	−3°·32
Ammonium Chloride	$NH_4Cl = 53{\cdot}4$	0°·0653	−3°·48
Sodium Bromide	$NaBr + 4H_2O = 174{\cdot}6$	0°·0189	−3°·30
Potassium Bromide	$KBr = 118{\cdot}8$	0°·0292	−3°·47
Sodium Iodide	$NaI + 4H_2O = 221{\cdot}4$	0°·0152	−3°·35
Potassium Iodide	$KI = 165{\cdot}6$	0°·0212	−3°·51

With such regularities as are here exhibited, there can be no doubt that an intimate relation exists between the depression of the freezing point and the number of molecules in solution. But it is not clear whether the quantities under Q are identical with the molecular weights or are definite fractions of these values. If the amount represented by the formula NaCl be the true molecular weight of common salt, then the other quantities under Q must also represent the molecular weights of the several compounds.

But if Q be twice or thrice as great, a similar conclusion must be arrived at. This method, therefore, still leaves some room for doubt as to which value must be accepted, and this uncertainty becomes greater as in the case of some salts smaller and for others larger values for E Q are obtained; thus, for example, for the so-called vitriols, the following results have been obtained:

—	Q	E	E Q
Epsom Salts .	$MgSO_4 + 7H_2O = 245{\cdot}9$	0°·0072	1°·77
Zinc Sulphate .	$ZnSO_4 + 7H_2O = 286{\cdot}7$	0°·0058	1°·66
Nickel Sulphate .	$NiSO_4 + 7H_2O = 280{\cdot}1$	0°·0055	1°·54
Copperas . .	$FeSO_4 + 7H_2O = 277{\cdot}4$	0°·0055	1°·53
Blue Vitriol . .	$CuSO_4 + 7H_2O = 248{\cdot}8$	0°·0065	1°·62

By simply doubling the quantities Q, these results might be brought into agreement with those above. In the case of other compounds, however, such agreement could not possibly be brought about by these simple devices.

It has been found by F. M. Raoult that organic substances examined by this method give much more uniform results than inorganic salts. This knowledge is all the more valuable, as the molecular weights of many of these bodies can be determined in the state of vapour (§ 21). Thus, for example, the reduction of the freezing point, brought about by one part by weight of ether, $C_4H_{10}O = 73{\cdot}84$, in 100 parts of water gives a value for E of 0°·23. If the molecular weight of ether (73·84) be dissolved in 1,000 parts by weight of water, then the molecular depression E Q is equal to $\cdot 023 \times 73{\cdot}84 = 1^{\circ}{\cdot}7$; a number which agrees satisfactorily with the molecular depression for the vitriols. Similar values are obtained for many other organic compounds, as shown by the following examples:

—	Q	E Q	—	Q	E Q
Glycerol .	$C_3H_8O_3$	1°·71	Lactic Acid .	$C_3H_6O_3$	1°·92
Mannitol .	$C_6H_{14}O_6$	1°·80	Malic „ .	$C_4H_6O_5$	1°·89
Invert Sugar .	$C_6H_{12}O_6$	1°·93	Tartaric „ .	$C_4H_6O_6$	1°·95
Milk „ .	$C_{12}H_{24}O_{12}$	1°·81	Citric „ .	$C_6H_8O_7$	1°·93
Cane „ .	$C_{12}H_{22}O_{11}$	1°·85	Urea . . .	CH_4N_2O	1°·72

This discovery is of great importance, since by its aid we can determine, at any rate in terms of certain standards, the molecular weights of those substances to which on account of their lack of volatility Avogadro's law cannot be applied. Thus, for instance, for a long time some doubt existed as to whether the molecular weight of milk sugar was equal to or was double the molecular weight ascribed to grape or fruit sugar, the mixture of which forms inverted sugar. The above numbers, however, remove this doubt and show that the molecular weight of milk sugar cannot be represented by the formula $C_6H_{12}O_6$, for this amount would only correspond to a depression of 0°·9 C.

Raoult has also found that the solutions of other solvents besides water obey similar laws.

If equal weights, *e.g.* 1 gram of different substances be dissolved in 100 or 1,000 grams of one and the same solvent, then the depression in the freezing point of the solvent is found to be approximately proportional to the molecular weights of the dissolved bodies. From this it follows that the product of the depression into the molecular weight is practically the same for all the dissolved substances. This 'molecular depression,' as the product is styled, is usually calculated from the depression produced by 1 gram of substance in 100 grams of solvent. This product would, therefore, represent the depression produced by the gram molecular weight dissolved in 100 grams of solvent, provided that Raoult's law applied to solutions of such concentration. But as this law is only applicable to very dilute solutions, this product has only a real significance in the case of substances of very low molecular weight. Consequently it would be more satisfactory to define the 'molecular depression' as that produced by the gram molecular weight dissolved in 1,000 grams of solvent—*i.e.* a tenth of the above value, a quantity which in the majority of cases can be actually observed.

The 'molecular depression' depends mainly upon the nature of the solvent, and only to a minor degree on the properties of the dissolved substance. It is influenced by the concentration of the solution, and in many cases this influence is considerable. The rule is to employ the values based upon observations made with very dilute solutions, or values for an infinitely dilute solution deduced by extrapolation from a series of observations.[1] If this value has been ascertained for a given solvent from the freezing points of the solutions of several substances of known molecular weight, then it may be employed for the estimation of unknown molecular weights. If by dissolving p parts by weight of a given substance in P parts by weight of the solvent the freezing point is depressed by 'e' degrees, then the depression E produced by 1 part in 1,000 parts by weight of the solvent is obtained from the following proportion:

$$e : E :: \frac{p}{P} : \frac{1}{1000}; \quad E = e \times \frac{P}{1000 \, . \, p}.$$

If A be the molecular depression of the solvent, then according to Raoult's law we have the following:

$$m \, . \, E = A; \quad m = \frac{A}{E} = \frac{e \, . \, P}{1000 \, . \, A \, . \, p}.$$

The molecular weight m is obtained by dividing the constant A by the depression E, produced by 1 part in 1,000 parts by weight of the solvent. The number obtained in this way must be corrected by the stœchiometric values (*v.* § 24).

The constant A is related to the molecular weight m of the solvent in accordance with a definite law. Raoult's supposition that both values are inversely proportional to one another—a conclusion based on his earlier experiments—has not been confirmed. Van't Hoff, on the other hand, from theoretical considerations has concluded that the molecular depression must be inversely proportional to the latent heat of fusion of the solvent and directly proportional to the square of the absolute temperature of its melting point. The equation

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[1] Many observers have in their calculations employed observations made with a one per cent. solution instead of 1 in 100, which is of course not quite the same, yet may be employed to yield the depression for a solution of infinite dilution.

$$A=0{\cdot}002\times\frac{T^2}{W}\,[1]$$

in which T represents the absolute temperature of the melting point and W the latent heat of fusion, has been submitted by Eykmann to an experimental investigation, and has been found to hold for a large series of solvents. When T and one or other of the values A or W are known, then by the aid of Van't Hoff's equation the remaining number may be calculated, and, as the following table shows, the calculated values approximate satisfactorily to the observed. The calculated values for W are deduced from the observed values for A, and conversely the calculated values for A are deduced from the observed values of W. In addition to the absolute melting point T, the molecular weight of the solvent is given under M.

Solvent	M.	T.	W.		A.	
			Obs.	Calc.	Obs.	Calc.
Water	18	273°	79c	80c	1·85	1·89
Formic Acid	46	282°	55·6	56·5	2·77	2·84
Acetic Acid	60	290°	43·2	43	3·86	3·88
Benzene	78	278°	29·1	29·4	5·00	5·30
Urethane	89	321°	40·8	41	5·14	4·96
Phenol	94	313°	25	26	7·4	7·7
p-toluidine	107	312°	39	38·6	5·1	4·9
Nitrobenzene	123	278°	22·3	21·6	7·07	6·95
Naphthalene	128	353°	35·5	35·7	6·90	6·94
Thymol	150	323°	27·5	27·9	8·32	7·39
Diphenyl	154	344°	28·5	29·4	8·35	7·94
Azobenzene	182	340°	29	29·4	8·35	7·76
Ethylene dibromide	188	283°	12·9	13·2	11·8	11·9
Lauric Acid	200	316°	43·7	44·9	4·4	4·5
Palmitic Acid	256	323°	50	50·4	4·4	4·4

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[1] In the ordinary calculation on 100 parts of solvent the equation is naturally

$$A=0{\cdot}02\frac{T^2}{W}.$$

It is evident that A in the majority of cases increases with increase in the molecular weight. Further, there is a satisfactory agreement between the observed values of A and W and those calculated by the formulæ of Van't Hoff. In fact, in some cases W was first calculated and the value has been subsequently proved to be correct by the observations of O. Pettersson.

§ 79. **Exceptions to Raoult's Law.**—For many substances in aqueous solutions Raoult's law is not applicable. This is especially true of many acids and salts, the smallest amount of which represented by the stœchiometric formula depresses the freezing point of water much more than the molecular weight of any indifferent organic substance, in some cases the depression being twice as great. According to the above table, for instance, a solution of 58·37 grammes of common salt in a litre of water freezes at − 3°·5, whereas a solution containing 341·2 grams of cane sugar ($C_{12}H_{22}O_{11}$) would freeze at −1°·85. Common salt, therefore, behaves as though it were composed, not of an amount represented by the formula NaCl, but by an amount almost equivalent to two molecules. To explain these facts S. Arrhenius has suggested that the greater portion of the salt exists in solution dissociated into sodium and chlorine. A somewhat similar proposal was formerly made by Clausius to explain the decomposition of its solution in electrolysis (compare §§ 12 and 99).

Improbable as this hypothesis may at first sight appear, very weighty arguments have been advanced in support of it.

§ 80. **Diffusion.**—If the composition of a solution is different in different parts, then, even when the temperature throughout is the same, there arises without any external cause a gradual adjustment, inasmuch as all the constituents of the solution are gradually and uniformly distributed throughout the mass.

The movement by which this uniform distribution is effected was styled 'diffusion' by Graham. This diffusion takes place slowly, and consequently the substances mixing with one another may often take weeks and perhaps months in passing through a distance of a few decimetres only. Inasmuch as this admixture takes place spontaneously, it must result from the motion of the particles in the liquid state, and must also take place in perfectly homogeneous and uniformly mixed liquids.

The difference between this case and that in which the mixture is not uniform is to be found in the fact that, as each of the particles in any given position moves in one direction, an equal number of particles will move in the opposite direction; whereas in the case of mixtures lacking this uniformity, from that portion of the liquid containing a larger number of particles in a given space more particles will come in consequence of this excess, assuming that the temperature, and, consequently, the velocity of the particles on both sides, are equal. The uniform distribution of the concentration will therefore occur the more readily the greater the difference in the contents of the two layers of liquids in contact with each other.

From the large amount of heat which is rendered latent in the passage from the solid into the liquid state one may conclude that the liquid particles have considerable motion imparted to them. That these particles, despite this motion, only move slowly from one position to another may arise from the fact that they interfere with one another's free movement, and, consequently, only with great difficulty and very slowly are they able to force their way through the crowd of surrounding particles.

The velocity with which a substance diffuses depends not only upon its nature, but also upon the nature of the solvent, and, further, upon the temperature. These phenomena have been chiefly investigated for aqueous solutions. One might at first be inclined to believe that the smaller and lighter particles would diffuse more rapidly than the larger and heavier particles. Whilst this frequently is the case, it does not obtain universally; and especially is this found not to be so with bodies which are very nearly allied to one another. In illustration of this a comparison may be made by taking an equal number of molecular weights of different substances dissolved in an equal volume of the same solvent. For instance, if the weight in grammes of potassium chloride, 74·4, represented by the formula KCl, of common salt the amount 58·37, of lithium chloride the amount 42·38, represented by their respective formulæ, be dissolved in a litre of water, and the several solutions brought in contact with pure water, then, by determining the quantities of each which pass in equal times under otherwise similar conditions into the water, we obtain values for the diffusion of these different substances, which may be compared with one another. Experiments of this character conducted by J. H. Long have shown that the number of molecular weights of each of these bodies which diffuse in equal times are represented by the values given under *d* in the following table:—

—	*d*	—	*d*
KCl = 74·4	803	KNO_3 = 100·9	607
$NaCl$ = 58·4	600	$NaNO_3$ = 84·9	524
$LiCl$ = 42·4	541	$LiNO_3$ = 68·9	512
KBr = 118·8	823	KI = 165·6	823
$NaBr$ = 102·8	509	NaI = 149·5	672

These examples show that potassium salts, despite their greater molecular weights, diffuse more readily than the corresponding sodium compounds, and these latter more readily than the corresponding compounds of lithium. Such examples, which might be considerably increased, show that frequently the large molecules diffuse more readily than the small ones; still, on the other hand, there are substances having very large molecular weights, more especially complicated organic compounds, which diffuse with extraordinary slowness. The substances mentioned in the foregoing section diffuse at a comparatively rapid rate, and these bodies, according to the hypothesis advanced by Arrhenius, must be supposed to exist in their solutions in a state of dissociation.

§ 81. **Osmosis and Dialysis.**—If two liquids capable of diffusing into each other are brought, not into immediate contact, but are separated by a septum which is permeable to some of the constituents, but is impermeable, or only permeable to a less degree to the other, then we have produced that remarkable phenomenon to which Dutrochet has applied the term *osmosis*, from ὠσμός, an impulse. As this term implies, the liquid to which the septum is permeable is driven through in such a way that a considerable inequality of pressure on each side of the separating wall is produced. Substances which swell up when moistened (compare § 74) are the best adapted for such septa. Animal or vegetable membranes, parchment paper, gelatinous precipitates, such as copper ferrocyanide or tanned gelatine, and also caoutchouc and other bodies, are examples of the materials which may be used for such septa; still there are also many substances which act in a similar manner, although they do not swell up when moistened. But what may and what may not pass through such septa is determined by the nature of the septum itself and also of the liquid. The cuticle of plants and animals and also many membranes which are produced from aqueous solutions are permeable by water, but are impermeable or only slightly permeable to many substances soluble in water. Caoutchouc does not allow water to pass through it, although many organic substances diffuse readily through this material.

The most remarkable fact observed in connection with the phenomena of osmosis is that the portion of the liquid by which the wall is permeated will force its way through the membrane, despite the greater pressure existing on the opposite side. For instance, supposing an aqueous solution of salt be separated from pure water by a membrane permeable only to water; still, as has been shown by Nollet in 1748, and later by Fisher, Magnus, Dutrochet, and others, the water passes through the membrane to the salt, so that on the salt side an increased pressure is produced. The water therefore moves in opposition to the pressure which has been produced by its own movements. As soon, however, as the pressure reaches a certain amount, then this increase in volume ceases. This maximum pressure, the so-called 'osmotic pressure,' has been studied and measured for different substances by W. Pfeffer, and in many cases has been found to be very considerable and to be proportional to the concentration of the solution. At one time it was believed that this pressure was due to the attraction of the salt or other dissolved solid for the water. This explanation is no longer permissible, for De Vries has found that in a very large group of substances this pressure for the solution of two different substances is approximately the same when both solutions contain in equal volumes an equal number of molecules of the dissolved bodies. De Vries did not measure the 'osmotic pressure' directly, but determined the concentration of those solutions of different substances which give up as much water to certain plant cells as they receive from the membranes of these cells. These solutions are spoken of as *isotonic* (from *ἴσος*, equal, and *τόνος*, pressure). De Vries found that in order that the solutions of those organic substances investigated by him should be isotonic, they must contain in equal volumes an equal number of molecular weights, whilst solutions of inorganic salts were found to be isotonic with the former when less concentrated. Consequently very different substances exert equal osmotic pressures; the phenomenon, therefore, cannot be altogether dependent upon the material composition of the bodies nor upon an attraction they exert on water. It is improbable that this attraction should be the same for substances so very different from each other.

We cannot therefore accept such an attraction to explain this phenomenon. If on one side of the wall there were water particles only, and on the other, particles of another substance, for instance, sugar, for which the wall is not permeable, then upon this side the number of water particles coming in contact with the wall would be smaller the smaller their number, and consequently the larger the number of particles of sugar contained in a unit volume. The smaller the number striking the wall so much the smaller will be the number passing into and through the wall. It may occur that the membrane swells up more in water than in solutions of salt or sugar, and therefore for this reason more water will pass on to the side on which the water is. Consequently a smaller number of particles of water pass from this sugar solution towards the pure water than from the water to the sugar solution; the amount of water on the side of the sugar solution must therefore increase. If the water so passing through the wall can flow away in any other manner, then the passage will continue so long as the concentration on both sides of the wall remains unequal. If, however, the solutions are contained in closed vessels, then in consequence of the advent of the water the pressure will be increased. In proportion as this increase proceeds the amount of water passing through the wall in a given time diminishes, and will finally cease when the pressure has reached a certain maximum; then the interchange ceases entirely. This arises from the fact that the pressure produced by the water particles is more strongly exerted upon the wall, and consequently they press through it. In this way the equilibrium of the materials passing from both sides is established.

If the pressure be increased artificially above this maximum then more water passes out than is returned, till the equilibrium is again established.

This osmotic pressure is dependent upon the condition of the wall, and not alone upon its composition, but also possibly upon its thickness; for naturally it is easier to force the water through one kind of wall than it is for it to pass through another of a different material. If solutions of different substances are brought in contact with the same wall, then the osmotic pressure will always be the same when the solutions contain an equal number of molecules of the substances to which the wall is impermeable. If these two solutions are divided by a partition only permeable to the solvent, then no alteration in pressure is produced; if, however, one solution contains in a given volume more molecules than the other, then the pressure rises in this solution. The osmotic pressure as well as the depression of the freezing point may be used for the purpose of comparing and determining molecular weights. This method is, however, less convenient than the former, and suffers from the fact that these septa are, as a rule, not absolutely impermeable to dissolved substances.

By this method also it is found that acids and salts exhibit an exceptional behaviour similar to that described in § 79.

Van't Hoff has utilised Pfeffer's observations with membranes of copper ferrocyanide and aqueous solutions of indifferent substances, such as sugar, and has calculated from these the osmotic pressure, which he has shown has the same value as the pressure that the sugar would exert if it could exist in the gaseous state and occupied a volume equal to that of the solution. It does not necessarily follow that the sugar exerts this pressure in a condition analogous to that of a gas, for the osmotic pressure is produced by the passage of the water through the membrane, and it certainly would be arbitrary to neglect one constituent of a fluid mixture (the water) in order to regard the other (the sugar) as a gas filling an empty space. In this case both substances are liquids.

§ 82. **Evaporation and Ebullition.**—If a liquid be brought into a vessel which it does not completely fill, then, as a rule, a portion of the liquid passes as vapour into the space above. When this formation of vapour takes place only at the surface of the liquid it is styled 'evaporation,' but when it also proceeds in the interior of the liquid itself it is described as ebullition, or boiling. Which of these two forms of vaporisation obtains is determined by external conditions, especially by the pressure on the liquid and by the temperature. Evaporation may also take place from the surfaces of solid bodies.

When the space above the liquid is completely void, then, as a rule, evaporation takes place very quickly; but if it be filled with air or other gas the vaporisation proceeds more slowly. The mass of the vapour increases, but only until a maximum density is reached, that is, until every unit of space contains a certain definite weight of vapour: this maximum density is dependent upon the nature of the substance and also upon the temperature. This is true whether the space be filled with air or not. The vapour tends to expand, and consequently exerts a pressure on the walls of the vessel, which pressure with constant temperature is approximately, but not absolutely, proportional to the density. To this maximum density there is a corresponding maximum of pressure styled the pressure or tension of the saturated vapour. The maximum density is always reached when a sufficient amount of liquid is present. If another gas exist in the space with the vapour, then both exert a pressure, giving a total pressure equal to the sum of the two. The component pressures are spoken of as the 'partial' or 'individual' pressures.

When the space filled with a saturated vapour is reduced, and therefore the vapour compressed, neither the pressure nor the density is altered, but a portion of the vapour is converted into liquid and separates out as such. If the reverse happen, then an amount of vapour is formed until the conditions of the maximum of density and of pressure are again restored. It must not, however, be concluded that by reason of the impossibility of exceeding this maximum the production of vapour ceases when this condition has been reached, for the vaporisation continues; but as much vapour condenses and liquefies as there is fresh vapour formed. The condition of a saturated vapour therefore is no condition of rest, is not a statical but a dynamical equilibrium, a state of motion which has become stationary.

The maximum pressure of the vapour of a substance is determined by the material composition of the body and also by the temperature. At low temperatures it is frequently immeasurably small, whilst at higher temperatures it is considerable; still there are many bodies which cannot withstand the necessary rise of temperature without suffering decomposition, and therefore in the case of many liquids it is not known whether they can in any way be converted into vapour.

When the pressure of the vapour is as great or a little greater than the pressure surrounding the liquid, then the production of vapour proceeds, not at the surface alone, but also in the interior of the liquid itself, and the liquid boils. The formation of bubbles of vapour in the mass of the liquid itself does not necessarily take place as soon as the required temperature and pressure have been reached, just as the crystallisation of a solid from its solution does not begin immediately the condition of saturation has been reached. A liquid heated to a temperature above its boiling point is described as 'superheated.' This condition is analogous to that of supersaturation in the case of solutions. When the formation of vapour takes place in a 'superheated' liquid, it proceeds rapidly and suddenly, just as crystallisation in a supersaturated solution, and may consequently occasion violent explosions. Various agencies are found to be active in giving an impetus to the production of vapour—for example, shaking —but perhaps the most effectual is the contact of solid bodies, the surfaces of which are covered with a very thin layer of air or gas, or a solid which forms a gas when brought into the liquid will also promote the production of vapour. In this thin layer of air the first vapour production takes place, which rapidly extending forms a larger bubble, into the interior of which evaporation takes place from all sides. Bodies which condense air easily upon their surface, like platinum, or porous substances containing air in the pores, like burnt clay, charcoal, &c., are specially active in promoting this production of vapour. The walls of the containing vessels, more especially those constructed of glass or porcelain, act in the same way, by reason of the thin layer of air which is retained adhering to their surfaces. If this layer of air has been removed either by strongly heating the vessel or by long continued boiling of the liquid in it, then sudden and violent ebullition may set in, which can be avoided by bringing into the liquid, platinum wire, sand, or pieces of clay pipe-stems, &c.

The nature of the relationship between vapour pressure and temperature is so far alike for all volatile substances that with a rise in temperature the pressure increases at first slowly, then rapidly and more rapidly, until at last the increase takes place with extraordinary rapidity. If these phenomena are represented graphically with the abscissæ for the temperature and the pressure as ordinates, then the curve is found to be convex to the axis of the abscissæ, and is at first almost parallel to this axis, and finally almost perpendicular to it. As yet such representations have been made in only a few isolated cases. The law underlying this relationship has not yet been completely elucidated. As a rule, it has been deemed sufficient to fix and determine the boiling points of different substances, *i.e.* the temperatures at which the liquids boil under the ordinary atmospheric pressure. But since this pressure varies from time to time, and is different in different places, such determinations are of little value unless the height of the barometer be also measured. For instance, in consequence of the higher position of Tübingen or Munich, the majority of substances boil 1° or 2° lower at these places than they do at Berlin or Königsberg.

§ 83. **Boiling Points.**—The comparison of the boiling points of substances of analogous composition has shown the existence of a very intimate relationship between the boiling point and the composition. These relationships were first brought to light by the investigations of H. Kopp and of H. Schroeder, and have since been amplified and extended by numerous investigators. It is chiefly amongst the organic compounds that such investigations have been made, and here it has been shown that regular changes in composition correspond to similarly regular alterations in the boiling points.

Among the numerous series of organic compounds of like atom-linkage (cf. § 47), the members of which differ from one another by CH_2, a difference of 13·97, or approximately 14 units, in their molecular weights, the boiling points and the molecular weights form arithmetical series with approximately equal differences; still the differences in the boiling points are not exactly equal, as is the case with those of the molecular weights.

The following examples are taken from the chlorides, bromides, iodides, alcohols, and acids derived from the series of so-called paraffins (hydrocarbons of the general formula C_nH_{2n+2}). The boiling points in each of the five series increase with the number of carbon atoms; still, this alteration is somewhat different in each series.

n	CHLORIDE $C_nH_{2n+1}Cl$	BROMIDE $C_nH_{2n+1}Br$	IODIDE $C_nH_{2n+1}I$	ALCOHOL $C_nH_{2n+1}OH$	ACID $C_nH_{2n}O_2$
1	−22°	+4°·5	40°	66°	100°
	35	34	32	12	19
2	+12°·5	38°·4	72°	78°·5	119°
	34	33	30	19	21
3	46°·4	71°	102°	97°·4	140°
	32	29	28	20	22
4	77°·9	100°	129°·6	117°	162°
	28	29	26	20	23
5	106°·6	129°	155°·4	137°	185°
	26	27	24	20	20
6	133°	156°	179°·5	157°	205°
	26	23	22	19	19
7	159°	179°	201°	176°	224°
	21	20	21	19	13
8	180°	199°	222°	195°	237° (?)

Greater differences are found among the more easily volatile substances than in the case of the less volatile members. Still, in the case of bodies of approximately equal volatility the increase is greater in one family than in another. In consequence the remarkable relation obtains that the iodides and bromides of the radicals C_nH_{2n+1}, containing a smaller number of carbon atoms, boil at a lower temperature than the hydroxyl compounds; whereas with higher values of *n* the iodides and bromides are less volatile than the alcohols. With increasing values of *n* the chlorides approximate more nearly to the alcohols; whereas when $n=1$ the alcohol boils 88° C. higher than the chloride, and when $n=8$ the difference is only 15° C.

Relationships between the boiling point and molecular weight similar to the above are exhibited in many other series. A. Winkelmann has shown that similar differences are observed whatever be the pressure at which the boiling point is determined: the smaller the pressure the smaller the differences.

These approximately regular differences in the boiling points are only found when the substances compared have similar atomic linkage. Even minute differences in this respect may give rise to considerable deviations in the boiling point. For instance, the 'normal' hydro-carbons, containing carbon atoms united in a single chain, must not be compared with their isomerides containing side-chains of carbon atoms: the former boil at considerably higher temperatures than the latter. Inasmuch as by the replacement of hydrogen by an elementary atom or radical the volatility is affected, and the extent and manner of this alteration are determined by the position of the hydrogen so replaced, those compounds can alone be regarded as homologous in which there is complete analogy in the position of the substituting elements or groups. It is, in fact, this far-reaching influence exerted by the mode of the atom linkage on the boiling point which has made the volatility of compounds of great service in the investigation of the linking of the atoms in different compounds. Organic chemistry provides numerous illustrations of the application and value of this method of determining the constitution of compounds.

§ 84. **Vapour Pressure of Mixed Liquids.**—If several liquids are contained in the same vessel, each of these will give off vapour into the part not occupied by the liquid. Regnault has shown that in such cases the phenomena may be divided into three distinct classes.

When liquids do not mix with one another, then each constituent gives off as much vapour as if it existed alone, and the total pressure is equal to the sum of the partial pressures of the vapours of both. Therefore a mixture of two such liquids will boil at a lower temperature than either of the constituents. For instance, if water be poured on to bromoform ($CHBr_3$), which boils at 151° C., then ebullition commences at the surface separating the two at a temperature of 93° C., because at this temperature the sum of the vapour pressures of water and of bromoform is sufficient to overcome the pressure of the atmosphere. The boiling point remains constant so long as there is a sufficient quantity of each liquid present. Carbon bisulphide and water, ethyl iodide and water, and many other combinations behave in a similar manner. This property may lead to very considerable error in the determination of boiling points. Thus, ethyl iodide in presence of a little water will boil 10° C. lower than the pure substance.

When liquids mix only to a limited extent with each other—as, for instance, ether and water (*vide* § 75)—then the vapour pressure of the mixture is less than the sum of the pressures of the single constituents, and, in fact, is only as great as that of the more volatile constituent; in the instance cited it would only be as great as that of ether. In such cases the boiling point of the more volatile liquid could be correctly determined in presence of the other. The more volatile component having distilled over with a portion of the less volatile liquid, the boiling then ceases, to commence again when the temperature at which the latter boils has been reached.

When liquids mix in all proportions, the vapour pressure of each reduces that of the other, so that the pressure of the mixture is considerably less than that of the more volatile constituent, and lies between their separate pressures. The pressure in such cases varies very considerably with the proportion of the constituents. If such a mixture is distilled, then the boiling point gradually rises in proportion as the more volatile constituent distils over. Separation by distillation in such cases is much more difficult than in either of the above instances. Separation is then only possible when the distillation is frequently interrupted, as in fractional distillation, when the distillate as well as the residue are each separately redistilled.

§ 85. **Relation of Density and Pressure of Vapours to Molecular Weights.**—If a vapour be examined under a pressure much smaller than the maximum of its vapour pressure at the temperature of experiment, then it is found that Avogadro's law (§ 17) holds true for the vapour, *i.e.* equal volumes of different vapours contain the same number of molecules, and as many as are contained in the same volume of a gas, provided that gases and vapours alike are measured under the same conditions of temperature and pressure. Under these conditions the densities are proportional to the molecular weights, and may serve, therefore, for the determination of the latter in the manner already described in §§ 19–21.

When gases and vapours or several vapours are contained within the same space, and provided these gases and vapours exert no chemical action upon one another, and do not, when in the liquid state, mix with one another or dissolve in one another, then the sum of all the molecules is the same as would be the case were the space filled by a single gas or vapour under like conditions of temperature and pressure. In fact, the proportion of the pressure of each constituent to the total pressure is determined by the number of its molecules existing in the space. Methods for the determination of molecular weights have been based upon this property.

Thus, substances which cannot be heated without decomposing at the temperatures at which Avogadro's law can be applied may be mixed with indifferent gases, and the weight, pressure, and temperature of the mixture determined. Deducting from this the known or subsequently determined proportion of the admixed gas, the pressure and weight of the vapour are obtained, from which the density and molecular weight are calculated.

According to Alex. Naumann, the molecular weight of a volatile liquid can be determined by distilling it with another liquid with which it does not mix. For, in such cases, the pressure which each constituent of the mixture of vapour exerts is proportional to the number of its molecules in the vapour. The amount converted into vapour, and consequently that distilling over, is greater the larger the number and the greater the weight of the particles or the molecules. If P be the total pressure, and p and p_1 the partial pressures, *i.e.* the vapour pressures of each of the separate vapours, then

$$\mathrm{P} = p + p_1.$$

Further, let m and m_1 be the molecular weights and g and g_1 the weights of each substance distilling over; then

$$g : g_1 = pm : p_1 m_1.$$

If m_1 is already known and the pressure p_1 be measured for the temperature at which the mixture distils, then we have

$$p = \mathrm{P} - p_1, \quad m = \frac{p_1}{\mathrm{P} - p_1} \cdot \frac{g}{g_1} \cdot m_1.$$

For instance, from a mixture of toluene and water, 86·6 grammes of toluene and 21·1 grammes of water distil over at 84°·3 C. and 754·4 mm. At this temperature the pressure of aqueous vapour alone is 422·0 mm.; consequently we have—

$$\mathrm{P} = 754{\cdot}4 \text{ mm}, p_1 = 422 \text{ mm.}, p = \mathrm{P} - p_1 = 332{\cdot}4 \text{ mm.}$$

$$m = \frac{422}{332{\cdot}4} \times \frac{86{\cdot}6}{21{\cdot}1} \times 17{\cdot}96 = 94{\cdot}5.$$

The molecular weight of toluene, according to the formula C_7H_8, is 91·8. The agreement between these numbers is sufficiently satisfactory to leave no doubt as to the value of the molecular weight. This method can be used in many cases where others cannot be applied.

The vapour pressure may, according to Raoult, also be utilised to determine the molecular weights of substances in the liquid state. When a comparatively small amount of a solid or liquid is dissolved in a volatile liquid, such as ether, the vapour pressure of the solvent is thereby reduced and the reduction is almost proportional to the number of the molecular weights of the substance dissolved. For instance, the vapour pressure of ether is reduced almost by $\frac{1}{100}$ when 1 molecular weight of a substance is dissolved in 99 molecular weights of ether; with 2 molecular weights in 100, *i.e.* dissolved in 98 molecular weights of ether, the pressure is reduced by about $\frac{2}{100}$, and so on; still, the proportion of the substance dissolved must not be too great, otherwise this rule ceases to be reliable.

If f be the vapour pressure of pure ether, f' that of a solution containing g parts by weight of the dissolved substance in 100 parts of the solution, and consequently $(100-g)$ per cent. of ether, m the molecular weight to be determined, m_1 the molecular weight of ether ($C_4H_{10}O=73{\cdot}84$), and n the unknown number of molecules of the dissolved substance in 100 molecular weights of the solution, then the following proportion holds approximately :—

$$f' : f :: 100-n : 100;$$

and therefore

$$n=100\frac{f-f'}{f}.$$

Further we have also the following relations :—

$$g : 100-g=n\times m : (100-n).m_1,$$

and consequently

$$m=\frac{(100-n).g}{n.(100-g)}.m_1.$$

The molecular weights determined in this manner are only approximations and need correcting by the stœchiometric formula, just as do the molecular weights deduced from the vapour density.

Instead of the depression of the vapour pressure produced by the dissolved substance one can measure the proportional elevation of the temperature by which the vapour pressure is brought to its original height; or, in other words, the elevation of the boiling point by the dissolved substance may be determined. Based upon this view Beckmann has elaborated a convenient method for the determination of molecular weights.

The molecular elevation in the boiling point, which is produced by a molecular weight of a non-volatile substance dissolved in 1,000 parts by weight of the solvent, is dependent on the boiling point and the latent heat of vaporisation of the solvent, just as the molecular depression of the freezing point is influenced by the melting point and latent heat of fusion of the solvent. But it is convenient to determine the elevation for a series of bodies of known molecular weight, and to use the mean of the observed results for the purpose of calculating unknown molecular weights. In the following table are given Beckmann's determinations of the molecular elevation in the boiling point under a pressure of one atmosphere for a number of solvents. In column I. is the name of the solvent; in II. the approximated molecular weights; in III. the elevation as observed by Beckmann calculated on 1,000 c.c.; in IV. the same calculated on 1,000 grammes; and in V. the same calculated on 100 molecular weights of the solvent.

Solvent	M	Elevation of the boiling point for		
		1,000 c.c.	1,000 g.	100 M
Water	18	0°·54	5°·18	0°·288
Alcohol	46	1°·56	1°·15	0°·251
Acetone	58	2°·22	1°·67	0°·288
Acetic Acid	60	2°·69	2°·53	0°·422
Ether	74	3°·03	2°·11	0°·285
Carbon Bisulphide	76	1°·94	2°·37	0°·312
Benzene	78	3°·28	2°·67	0°·343
Ethyl Acetate	88	3°·14	2°·60	0°·296
Chloroform	119	2°·60	3°·67	0°·308
Ethylene Dibromide	188	3°·25	6°·31	0°·336

The mean elevation of the boiling point is about 0°·3 C. for one molecular weight dissolved in 100 molecular weights of the solvent.

§ 86. **Critical Temperature.**—As the pressure of a vapour increases with the temperature, and further, this increase per degree is greater the higher the temperature, it follows that the higher the temperature the greater will be the pressure required for the condensation of a vapour. For every vapour there exists a temperature above which no pressure, however great, can effect the liquefaction of that vapour. Andrews, the discoverer of this property, has styled this temperature the 'critical temperature,' and the pressure required to effect the liquefaction at temperatures a little below this is spoken of as the 'critical pressure.' There is a critical temperature for every vapour, provided it is not decomposed by the heat necessary to raise it to this temperature. The condition above this temperature is distinguished as the gaseous state from that of the vapour.

This discovery of Andrews indicated the method to be employed in the liquefaction of the so-called permanent gases, such as hydrogen, oxygen, nitrogen, carbon monoxide, marsh gas, &c., which Natterer had attempted but without success, although he had employed a pressure of several thousand atmospheres. These gases were first successfully liquefied by Raoult Pictet, who not only compressed the gases, but also at the same time cooled them to temperatures much below their critical temperatures.

According to the recently published investigations of Cailletet and Collardeau, the conclusions of Andrews require certain limitations, insomuch that the possibility of a liquid existing as such does not suddenly cease at the critical temperature, but only the sharp definition of the liquid from the vapour disappears, to be replaced by a misty, ill-defined intermediate layer. At a little above the critical temperature the liquid still remains denser, and therefore heavier than the vapour, and also possesses other properties than those belonging to the vapour. This difference between the liquid and gas disappears more and more as the temperature rises.

Despite this limitation the critical temperature, which is also known as the absolute boiling point, still remains an important and characteristic constant.

The critical temperatures of different substances are very different, varying with their nature and composition, as shown by the examples in the table below, in which the critical temperatures are given under the heading CT, and the critical pressure in atmospheres under CP.[1]

The temperatures much below zero are in all probability too low, since according to Wroblewski the hydrogen thermometer with which these observations were made yields results a few degrees too low. Some of the other values for the critical temperature are scarcely exact, as authorities differ in the values assigned to them.

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[1] Dewar (*Proc. Chem. Soc.* 1897–8, p. 146) gives the boiling point of liquid hydrogen as −238° C., and infers that the critical temperature is −223° C., and that the critical pressure will not exceed 15 atmospheres.

—	—	C T	C P
Hydrogen	H_2	below − 220°C.	?
Fluorine	F_2	−155°	25
Nitrogen	N_2	−146°	35
Carbon Monoxide	CO	−140°	35·5
Argon	A	−121°	50·6
Oxygen	O_2	−119°	50·8
Nitric Oxide	NO	−93°	71
Carbon Dioxide	CO_2	+32°	77
Nitrous Oxide	N_2O	+35°	75
Hydrogen Chloride	HCl	+52°	93
Hydrogen Sulphide	H_2S	+100°	92
Cyanogen	C_2N_2	+124°	62
Ammonia	NH_3	+130°	113
Selenuretted Hydrogen	SeH_2	+137°	91
Chlorine	Cl_2	+141°	84
Sulphur Dioxide	SO_2	+155°	79
Marsh Gas	CH_4	−74°	57
Ethylene	C_2H_4	+10°	51
Ethane	C_2H_6	+35°	45
Acetylene	C_2H_2	+37°	68
Amylene	C_5H_{10}	+192°	34
Benzene	C_6H_6	+281°	50
Methyl Chloride	CH_3Cl	+142°	76
Ethyl ,,	C_2H_5Cl	+183°	54
Propyl ,,	C_3H_7Cl	+221°	49
Chloroform	$CHCl_3$	+268°	55
Carbon Tetrachloride	CCl_4	+282°	58
Water	H_2O	+370°	196

The critical temperatures are higher for many other substances; for many of the metallic elements it is probably higher than any temperature that can be artificially produced.

The fact that no pressure, however great, should liquefy a gas at temperatures above the critical temperature finds its explanation in the probability that above this temperature the particles are in such rapid motion that they seldom if ever remain attached to one another, and the attraction of the particles exhibited as forces of cohesion or of capillarity is completely overcome.

This conception finds strong support in many other observations; for instance, the flow of liquids, capillarity, and other phenomena all show that the cohesion of fluids is gradually weakened by rise in temperature. That this should be the case is shown also by the fact that in the conversion of a liquid into vapour or gas, the higher the temperature so much the less heat is absorbed or rendered latent. At the critical temperature or absolute boiling point the latent heat of vaporisation is probably zero, or is at any rate extremely small.

§ 87. **Nature of the Gaseous State.**—It has already been shown (§ 20) that, according to the views generally accepted, the particles which in a liquid are more or less coherent, are in vapours or gases completely separated, and have free and independent motion. The fact that vapours and gases, unless under great pressure, fill a space many times greater than that filled by the liquid from which they are produced indicates that in the vaporisation or the conversion into gas the particles are separated widely from one another. It is known as the result of numerous observations that, apart from gravity and universal gravitation, the particles of matter can only act upon one another at extremely minute distances; the particles of a gas or vapour must therefore be beyond the sphere of mutual attraction. A body left entirely to itself will, however, continue to move on in a straight line with the velocity imparted to it unless deflected from this path by some external influence. This is assumed to be the case with the particles of a gas or vapour, and, as shown in § 20, the pressure of a gas can in every detail be satisfactorily shown to be a consequence of this rectilinear motion of the particles.

According to the kinetic theory of gases, the pressure is proportional to the density; since the larger the number of particles, so many more particles must strike the walls of the containing vessel. Further, the pressure is proportional to the square of the velocity of these particles, for the frequency and the force of the impacts must increase with the velocity. The pressure is found to be proportional to the absolute temperature of a gas: that is, to the temperature reckoned from − 273° C. (or more exactly from − 272°·6 C.); it follows, therefore, that the velocity of the rectilinear motion of the particles must increase in proportion to the square root of the absolute temperature. This velocity must be very great, because the momentum of every impact is proportional to the product of the velocity into the mass; but the latter is very small. Clausius has succeeded, by very ingeniously combining theoretical considerations with the results of observation, in determining these velocities in absolute measures, the calculations being based upon the following considerations.

The pressure of a gas is equal to the change of momentum of every single impact (*i.e.* to the product of the mass of the moving particle into the change of its velocity) multiplied into the number of impacts on any unit of area exposed to the pressure; again, the pressure may be measured by a column of mercury: that is, in terms of the action of the force of gravity on a column of this metal of a certain height and of a sectional area equal to the unit of area. Placing these two different measures of the pressure on opposite sides of an equation, we then obtain an expression of the relationship between the velocity of the particles and a value expressed in metres per second or any other convenient unit of measurement. The equation in any case contains still an unknown factor, the number of the particles, and also the unknown mass of an individual particle. But of these unknowns the product alone occurs, representing a measurable quantity, viz. the mass of the unit of volume of the gas.

In the above it is assumed that the velocity of all particles is alike; in reality this can never be the case, since by the collision of the particles the velocities will undoubtedly vary, as is the case with a large number of billiard balls colliding freely. There will, however, always be found a value for the velocity, which, supposing all the particles to be uniform, would produce the same pressure as the variable values of the real velocities. Clausius has calculated that this velocity (v) should be expressed in metres per second as follows:

$$v = 485_m \,.\, \sqrt{\frac{T}{d \,.\, 273^\circ}}.$$

In this expression T is the absolute temperature and d the density of the gas, air being the unit.

As the density of a gas has been shown in § 21 to be proportional to the molecular weight, we may replace d by the expression

$$d = \frac{m}{28{\cdot}87},$$

and then obtain the following as the relation between the velocity and the molecular weight:

$$v = 485_m \,.\, \sqrt{\frac{T}{273} \,.\, \frac{28{\cdot}87}{m}} = 158_m \,.\, \sqrt{\frac{T}{m}}.$$

In accordance with this formula the following numbers represent the velocities in metres per second of the particles of oxygen, nitrogen, and hydrogen at 0°C., *i.e.* T=273, and at the critical temperatures −119°, −146°, and −220° (?).

Oxygen	$v_0 = 461_m$	$v_K = 346_m$,
Nitrogen	$v_0 = 492_m$	$v_K = 288_m$,
Hydrogen	$v_0 = 1844_m$	$v_K = 953_m$.

The velocities, therefore, are considerable even at temperatures near those at which the gas may be liquefied, and at the freezing point the velocities are much greater, for instance, than the velocity of sound.

§ 88. **Constitution of Gases.**—Many of the different properties of gases, such as the constant expansive tendency, their rapid filling of empty spaces, and many other qualities, find an easy and simple explanation in the great velocities of gaseous particles. On the other hand, at first sight many of the properties do not appear to be consistent with so great a velocity. In opposition to the acceptance of these views it has been pointed out that the mixing or diffusion of gases should be almost instantaneous; but although the mixing of the gases takes place more rapidly than in the case of liquids, it is still comparatively slow, so that even with small quantities of different gases their complete admixture may require hours and in some cases even days. This apparent contradiction is, however, entirely due to the conception that, in consequence of the great velocity of the particles of gases, the admixture of gases should be effected instantly.

Clausius has, however, shown that the tardiness of gaseous diffusion and the low conductivity for heat and other properties of gases may be satisfactorily explained, despite the velocity of the particles. A single particle which, if alone, would move through several hundred metres in a second, is retarded by others which it meets in its path, and colliding with these is reflected back just like an elastic ball, in the same way that a man running rapidly would be retarded as soon as he came into a throng. The crowding together of the gaseous particles cannot, however, be so great, for a comparison of the density of gases and liquids shows that the particles of a gas fill only a thousandth of the space taken up by the mass; consequently in the spaces between them there must exist for their movements to and fro a thousand times as much space as that filled by the mass. But at the same time the average distance between the particles can only be very small when their number is great and the mass of each correspondingly small. Starting with these assumptions from the known rate of diffusion, the conductivity for heat, the internal friction of gases, &c., the average distance which a particle must travel before it collides with a second has been calculated—this distance Clausius has styled the mean free path.

The length of path is shown to be extremely small in the case of gases at normal pressure—less, in fact, than any length microscopically visible. With the majority of gases at the average temperature and a pressure of an atmosphere the distance is less than the ten-thousandth part of a millimetre. With a velocity of several hundred metres per second the number of times which a given particle must collide with others is quite inconceivable, and, according to calculation, it must be from four to ten thousand million times per second.

These calculations show the subdivision of matter in the gaseous state to be excessively great, since at the average temperature and under the pressure of one atmosphere a cubic centimetre of any gas will contain approximately some twenty trillion particles. As the weight of this mass can be determined, and, in fact, is known, the weight of a single molecule may be approximately ascertained. The weight of a molecule of hydrogen has thus been found to be

0·000,000,000,000,000,000,004 milligramme;

or a quadrillion particles of hydrogen would weigh about four grams. Although these numbers cannot lay claim to any special accuracy, still they serve to give some idea of the magnitude (or, rather, the minuteness) of molecules and of atoms also.

Not only the weight but also the dimensions of the particles may be similarly estimated. The hindrance to its free movement experienced by a particle produced by collision with others is determined, not only by its velocity, but also by its dimensions; for the larger the particles the more they will interfere with one another. The path, therefore, will be shorter the larger the particles. The knowledge of the frequency of their collisions may further serve to enable us to form an estimate of and to measure approximately their dimensions. According to the calculations of O. E. Meyer, a cubic centimetre of hydrogen measured at 20° C. and under pressure of 760 mm. contains so many molecules that if they were laid side by side they would cover 9,500 square centimetres, or very nearly a square metre. Accordingly for each twenty trillion particles but a very small surface would be required, for in the length of a millimetre some four to five million particles could be arranged in a series.

The relative size of the molecules of two different gases or vapours may be calculated with greater exactness than can their absolute dimensions. By such calculations it has been shown by the author that in the case of most substances the actual spaces filled by the gaseous particles stand to one another approximately in the same proportions as that which obtains in the liquid state.

§ 89. **Boyle's Law.**—The behaviour of gases under all conditions is determined by the dimensions, the mass, and the velocity of the particles. The deviations from the fundamental laws of gases exhibited in individual cases can be explained in a satisfactory manner as arising from these several influences. According to Boyle's law, the volume of a given mass of gas is inversely proportional to the pressure upon it, and therefore the product of the pressure into the volume or the quotient of the pressure and density remains constant. This law is not, however, absolutely true of any gas; for every gas, with the single exception of hydrogen, exhibits a greater diminution in volume with increase in pressure than should be the case if the law were absolutely true, *i.e.* the value of the product P V diminishes. So soon, however, as the pressure increases to a considerable number of atmospheres then the value of the product P V becomes greater, arising from the fact that the volume decreases less rapidly than the pressure increases. Hydrogen as far as it has been investigated always shows this increase in the value of the product P V, and not the diminution. The first of these deviations from the theoretical laws is explained by the assumption that the particles of the gas at temperatures much above that at which liquefaction takes place mutually attract each other, an action which becomes more apparent the more frequently the particles strike one another. The deviation in the opposite direction finds its explanation in the reduction by increased pressure of the space between the particles, and not of that occupied by the particles themselves. The proportion which the latter bears to the total space occupied by the gas increases with the pressure.

Van der Waals has shown that the same causes which produce both these deviations from Boyle's law also account for the deviations from the following laws: '*The volume occupied by a gas varies directly as the absolute temperature. The pressure of a gas at constant volume is proportional to the absolute temperature.*'

The kinetic theory of gases, although it still requires further extension and further experimental investigation, is capable of giving a very satisfactory explanation of the behaviour and properties of gases; consequently this theory, in opposition to which at first many facts were cited, has now received general acceptance and recognition.

§ 90. **Mixture of Gases. Diffusion. Effusion. Transpiration.** When two or more gases come in contact with one another, each flows into the space filled by the others, even when they are both under the same pressure. The origin of this mixing or diffusion is the exceedingly great velocity of the particles, which, as already mentioned in § 88, despite its magnitude, can only effect a slow and gradual admixture on account of the frequent collisions of the particles with one another. The diffusion takes place most quickly with gases of small molecular weight, the particles of which have consequently greater velocities. In this respect hydrogen far exceeds all other gases; the rate of diffusion depends also upon the dimensions of the particles of the several gases themselves; since they form the barrier opposed to the free movement of the gaseous particles. It follows, therefore, that for any particular gas the nature of the gas into which it diffuses is important, and its rate of diffusion, therefore, is determined by the nature of the other gas.

When the surface separating the two gases is relatively large then the pressure, being the same on both sides, remains unchanged during and after the mixing of the gases. If the gases are separated by a porous partition or by a partition with a small opening, then the pressure will rise on the side towards which the gas with smaller molecular weight diffuses, because the other gas cannot pass through at a rate sufficiently great to compensate for the inequality of pressure. In course of time, however, this difference in pressure disappears.

In the flow of gases through narrow tubes or channels, which Graham styled 'transpiration,' the internal friction comes into play, and this being dependent upon the free path of the particles may be utilised for the purpose of determining the same.

The flow through a narrow opening in a very thin wall, described as 'effusion' by Graham, takes place with velocities which are inversely as the square root of the densities, and are consequently proportional to the velocities of the rectilinear motion of the particles. This property may therefore, as was proposed by Bunsen, be utilised to measure these velocities and also to determine the molecular weights.

§ 91. **Mixtures of Gases and Liquids. Absorption of Gases.**—When a gas comes in contact with a liquid, then, as a rule, the gas passes into the liquid as it would into a vacuum or a space already filled by another gas, whilst at the same time the liquid evaporates to some extent into the gas. The taking up of the gas by the liquid is spoken of as *absorption* when there is no chemical action between the two. It is, however, frequently difficult, if not impossible, to draw a sharp line of distinction between absorption and chemical combination. The solution of a gas in a liquid is spoken of as absorption when it takes place in accordance with Henry's law, *i.e.* when it is proportional to the pressure of the gas, and is described as chemical combination when it is independent of the pressure. There are many instances which stand midway between these two extremes, in which whilst the amount of gas absorbed varies with the pressure it is not proportional to it. Such cases will be considered later in the discussion of chemical change (§ 92 *et seq.*).

True absorption, which is proportional to the pressure, takes place very slowly when the gas is in simple contact with the surface of the liquid. When the two are brought into more intimate contact by shaking, then the absorption takes place rapidly. The absorption of the gas by the liquid proceeds until a certain relation between the density of the gas absorbed and that of the unabsorbed gas is reached, at which point equilibrium between the particles of gas absorbed and passing out of the liquid is maintained. This relation is called the *coefficient of absorption*: it is dependent upon the nature of the gas and of the liquid, and also upon the temperature. Many liquids—as, for example, mercury, and possibly other molten metals (perhaps with the exception of silver, which absorbs oxygen)—are practically impervious to gases; others absorb but little; whilst others, again, are capable of absorbing considerable proportions of gases. The following table contains the coefficients of absorption by water of several gases at 0° C., 10° C., and 20° C., as found by Bunsen (B.), and L. W. Winkler (W.):

—	—	0° C.	10° C.	20° C.
Hydrogen . . .	W.	0·0215	0·0203	0·0195
Nitrogen . . .	,,	0·0235	0·0193	0·0166
Carbon Monoxide . .	,,	0·0354	0·0292	0·0249
Oxygen	,,	0·0489	0·0394	0·0333
Marsh Gas . . .	B.	0·0545	0·0453	0·0376
Nitric Oxide . . .	W.	0·0738	0·0592	0·0505
Olefiant Gas . . .	B.	0·2563	0·1904	0·1597
Nitrous Oxide . .	,,	1·3052	0·9532	0·7191
Carbon Dioxide . .	,,	1·7967	1·2281	0·9674

These numbers show that the quantity of gas taken up by a unit volume of water is in some cases greater, in others considerably less, than is contained in an equal volume of the free gas itself. In the case of hydrogen the amount of gas absorbed by the unit volume of water is about 2 per cent. of the quantity of hydrogen contained in the unit volume; in fact, this proportion is maintained for parts by weight or for volume, assuming that in the latter case the volumes are measured under the same conditions of pressure and of temperature as those at which the absorption takes place.[1]

A litre of water at 10° absorbs only 20·3 c.c. of hydrogen, 19·3 c.c. of nitrogen, 39·4 c.c. of oxygen, but takes up as much as 1228·1 c.c. of carbon dioxide.

A comparison of the coefficients of absorption with the critical temperatures given in § 86 shows that the order is very nearly the same, and therefore those gases which require for their liquefaction the greatest cooling and pressure are the least easily absorbed by water. Absorption of gases by liquids would therefore appear to be a phenomenon analogous to that of their liquefaction.

Absorption would appear, therefore, to proceed as follows: a certain fraction of the gaseous particles coming in contact with the liquid is taken up by the liquid, the proportion being the greater with those gases which are the more easily liquefied. On the other hand, a portion of the gas is always given off again, and equilibrium is established when as much passes out as is taken up by the liquid. If the pressure on the gas is increased, then so many more particles impinge on the liquid in a given time, and consequently more is absorbed; when the pressure is reduced, then more particles pass out than in, until a new condition of equilibrium is established.

From a mixture of gases each gas is absorbed as though it alone were present, and therefore in proportion to its coefficient of absorption and its share of the total pressure, which Bunsen has described as the 'Partial Pressure.'

§ 92. **Chemical Change.**—The phenomena discussed in the foregoing sections are concerned with changes affecting the aggregation of molecules, but not of the molecules themselves, in which the nature of the atoms entering into their composition undergoes a change. The changes in composition of the molecules themselves form the true chemical phenomena, or, as they are usually styled, 'chemical interactions.' Every element in every compound is capable of such change, but in varying degrees. This power to resist such changes is styled stability and varies within the widest limits. In some substances the atoms are in a state of unstable equilibrium, such that the slightest change alters their arrangement; consequently these compounds retain their individuality only under very special conditions. Others, again, offer remarkable resistance to attempts to alter their composition; in such the atoms are so firmly united that they effectually resist the most powerful attempts to disturb their equilibrium. Between these extremes every possible and conceivable state of stability and instability is known.

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[1] For practical reasons Bunsen, and also Winkler, measure all the gas absorbed at 0°; consequently their coefficients at 10° and 20° would differ somewhat from those given in the table on p. 169.

Chemical changes may assume different forms, characterised by the alterations in the molecules produced by the changes.

(1) A molecule may be formed by the immediate union of the atoms (pure synthesis).

(2) Or it may be resolved into atoms.

(3) Two or more molecules may combine to form a single molecule. When the molecules are alike, the phenomenon is spoken of as polymerisation; *e.g.*

$$\underset{\text{3 mols. of aldehyde}}{3C_2H_4O} \quad = \quad \underset{\text{1 mol. of paraldehyde.}}{C_6H_{12}O_3}$$

When the molecules are different, the combination is described as 'addition,' *e.g.*

$$\underset{\text{Mercury}}{Hg} \quad + \quad \underset{\text{Chlorine}}{Cl_2} \quad = \quad \underset{\text{Corrosive sublimate.}}{HgCl_2}$$

$$\underset{\text{Ethylene}}{C_2H_4} \quad + \quad \underset{\text{Bromine}}{Br_2} \quad = \quad \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}$$

(4) On the other hand, a molecule may split up into several others, either like or unlike. The change when permanent is described as 'decomposition,' and as 'dissociation'

when the products of decomposition reunite on withdrawal of the cause producing the change.

(5) A substance may withdraw a constituent from another substance, or expel a constituent and take its place. The following changes,

$$HgBr_2 + Cl_2 = HgCl_2 + Br_2; \quad Cd + HgCl_2 = CdCl_2 + Hg,$$

may either be interpreted as the expulsion of bromine by chlorine, of mercury by cadmium, or as the chlorine withdrawing bromine from mercury, and the cadmium withdrawing the chlorine. The replacement of a substance (*e.g.* bromine) by another (chlorine) is described as 'substitution' of the second in place of the first.

(6) The most frequent form of chemical change is that of 'double decomposition,' in which two substances mutually interchange some of their constituents, *e.g.*

$$HH + ClCl = HCl + HCl$$

$$HI + AgCl = HCl + AgI$$

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Nitric acid}}{HONO_2} = \underset{\text{Ethyl nitrate}}{C_2H_5ONO_2} + \underset{\text{Water.}}{HOH.}$$

Formerly, many of the changes belonging to this category were regarded as syntheses or additions, but such views are now regarded as erroneous, *e.g.*

$$\cancel{H} + \cancel{Cl} = \cancel{HCl}, \text{ or } H + Cl = HCl.$$

(7) Triple and even more complex interactions are not infrequent; *e.g.* the oxidation of carbon monoxide (according to Dixon), or of metals (according to Traube), by moist oxygen, the bromination of benzene by the agency of ferric chloride (according to Scheufelen), and even the solution of zinc in dilute sulphuric acid:

$$CO + O \vdots H_2 + O \vdots O + H_2 \vdots O + CO = CO_2 + H_2O + OH_2 + CO_2$$

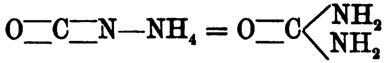
$$Zn + 2\ (OH \vdots H) + O \vdots O = Zn\ (OH)_2 + H_2OO$$

$$C_6\ H_6 + BrBr + FeCl_3 = C_6\ H_5\ Br + HCl + FeCl_2\ Br$$

$$HO \vdots H + Zn + H \vdots OSO_2\ OH = H.\ H + HO\ ZnOSO_2OH.$$

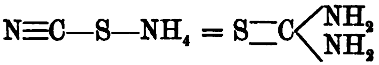
Considering the final result of the first change, one might conclude therefrom that oxygen and carbon monoxide alone take part in the action, since there is as much water present at the end as there was at the commencement. This view is nevertheless incorrect, as it has been shown that this oxidation does not take place in the absence of water, or, if at all, only at high temperatures.

(8) A re-arrangement of atoms may take place in the molecules themselves, resulting in a change of the atomic linkage; such cases are described as metameric changes, *e.g.*



$$O{=}C{=}N{-}NH_4 = O{=}C\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right.$$

Ammonium isocyanate Urea



$$N{\equiv}C{-}S{-}NH_4 = S{=}C\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right.$$

Ammonium thiocyanate Thio-urea

As a matter of fact, many of these main forms of chemical change frequently occur simultaneously; consequently the complete change may be a very complex one.

§ 93. **Causes of Chemical Change.**—Every chemical compound, if left to itself, would in all probability remain unaltered, retaining its composition and properties for all time. Alterations in composition may be produced by external causes of different kinds.

The following are the main forces active in effecting chemical changes: (1) mechanical disturbance, (2) heat, (3) light, (4) electricity, (5) the action of other substances; this last is usually ascribed to their powers of attraction or affinity. It is seldom that one or other of these causes is alone active; consequently it is difficult to distinguish and separate their individual effect. Heat is also concerned in such changes, for we are unacquainted with any means whereby all the heat may be withdrawn from a body; and, moreover, it is highly improbable that, supposing its particles perfectly motionless, a substance would still be capable of undergoing a chemical change.

§ 94. **Heat as Cause and Effect of Chemical Change.**—The relation between heat and chemical change is a very intimate one, so that not only is heat productive of chemical changes, but as a rule is a consequence of such actions, and is either positive or negative, according to whether in the change heat is produced or used up.

The mode of action of heat in producing and favouring chemical changes is easily understood; since heat consists of a rapid movement of particles not only of the molecules but also of the atoms composing them, it follows, therefore, that with the acceleration of this motion the atoms move farther and farther apart, and thus the coherence of the molecules is gradually loosened, and finally destroyed. It is not essential that the molecule should be thus broken down into single atoms; but these may, in consequence of the loosening of the already existing bonds, and their altered positions, find opportunities to enter into new states of combination, producing in this manner compounds more stable at the higher temperature than the original. In the case of more complex changes in which several substances take part, heat may, by loosening the bonds of union holding the atoms together, facilitate the action, and thus bring about the change, which might perhaps not have taken place without the aid of heat.

The mechanical theory of heat was at one time supposed to give a satisfactory explanation of the production of heat in chemical changes, this heat-production being regarded as due to the affinity, the force by which the atoms were supposed to be mutually attracted to one another. Assuming that the atoms are provided with these forces of attraction, which are only effective at short distances, then the atoms will obey these forces as soon as they are brought within the sphere of their mutual action, and will acquire velocities which will become greater the stronger the attraction and the smaller the mass to be moved. When the atoms clash with one another, then the kinetic energy must either become converted into heat or some other form of motion, or do work, *i.e.* move some mass under the influence of opposing forces. If heat is produced, then this will be greater in proportion to the strength of the active affinities, and this heat therefore should offer a very suitable means of measuring the strength of these affinities. When work is done, then, as a rule, this work consists in overcoming the forces of attraction of some other atoms, and consequently the atoms so held together are expelled. This very plausible theory was for a long time received as the true explanation, but was only tenable so long as no reliable method existed for measuring the strength of the affinities. So soon as it was possible to make such measurements it became evident that the greatest heat-production is not necessarily associated with the most powerful affinities, and therefore the calorific effect is not a suitable measure of the combining power. Further, it has been most clearly shown that the amount of heat produced depends upon the changes of state in each of the reacting substances, and not upon the reciprocal action of two bodies, and consequently not on their mutual affinity.

Since the early conception of the origin of the heat of combination must be abandoned, there only remains the hypothesis that this heat has its origin entirely or in part in the motion of the atoms, which they lose when combination takes place, and which must be imparted to them when this union is destroyed. It certainly may be assumed that this heat, at any rate in part, is the product of the forces of affinity; but such an assumption is at the present time quite useless, and only complicates the problem unnecessarily.

Inasmuch as the hope that the heat produced or used up in chemical changes might be utilised as a measure of affinity has not been realised, the investigations of these calorific actions declined in interest, but are now again becoming important, as the numerous results of observations in this field are studied and investigated free from and unprejudiced by preconceived notions, with the object of learning something of the changes in state which accompany chemical action.

§ 95. **Propagation of Chemical Change. Temperature of Ignition. Explosion.**—Whether a chemical change produced at any given point in a body or a mixture will spread throughout its mass depends as a rule not only upon the cause of the change, but also upon the heat produced by the action. For instance, supposing a mixture of a combustible gas and oxygen be heated at any given point by an electric spark, or any other means, to such a degree that the combustion begins, it does not necessarily follow that the burning will spread throughout the whole of the mixture. Whether it does so depends upon the amount of heat produced by the combustion. If this suffices to raise the adjacent layers of combustible material to the temperature required for its inflammation, *i.e.* to the 'temperature of ignition,' then these layers are burnt up, and in turn yield heat sufficient to ignite the next stratum, and so on until the whole is consumed. Since, however, in cases of this kind a portion of the heat produced is always given out either by radiation or conduction to the surrounding bodies not concerned with the reaction, it may happen that the progress of the combustion is interrupted before the entire mass has been attacked. This will be liable to occur when the temperature produced by the heat of combustion very slightly exceeds the temperature of ignition. In case the mixture contains non-combustible bodies, *e.g.* nitrogen, then, as such bodies have their temperatures raised at the expense of the heat produced by the combustion, the temperature is thereby reduced, and with a considerable admixture of such bodies the temperature may sink so low that the advance of the combustion ceases. Every combustible mixture may therefore be rendered non-inflammable by the admixture of a sufficient quantity of incombustible material. If no such disturbing influences are to hand, and the heat of combustion be great, then the heating may rise far above the temperature of ignition. Further, if the products of the combustion are gaseous or vaporous, then a considerable sudden expansion results, which may increase until it becomes an explosion.

Something of the same kind takes place in the case of substances which can be exploded by mechanical disturbance or by percussion. This property is alone exhibited by substances in which the atoms are in a state of more or less unstable equilibrium, from which condition they can pass with production of heat, or corresponding amount of work, into a more stable state of equilibrium. Examples of this class of bodies we have in the chlorine, bromine, and iodine compounds of nitrogen, in the organic nitrates and nitro-organic compounds. When such bodies yield gaseous or vaporous products of decomposition, and produce much heat, they may also act as explosives.

The liquid chloride of nitrogen, for instance, is decomposed by very slight causes; this decomposition is expressed by the following equation:

$$NCl_3 + NCl_3 = N_2 + Cl_2 + Cl_2 + Cl_2.$$

This action is attended by a considerable heat-production, and consequent marked expansion of its gaseous products. Glyceryl nitrate (commonly but erroneously described as nitroglycerine) $C_3H_5(ONO_2)_3$, in which $\frac{2}{3}$, or in reality $\frac{5}{6}$, of the oxygen is combined with the nitrogen, yields gaseous and vaporous oxidation products of carbon and hydrogen, whilst the nitrogen is also set free in the gaseous state. This decomposition can be brought about by percussion or detonation as well as by heat. If the nitrate be ignited in an open space, it burns slowly and quietly, for the gaseous products pass freely away. If the nitrate be enclosed so that this free passage is prevented, or if it be ignited by a powerful blow, then the violent shock and pressure produced will immediately decompose the particles near those first struck, and thus the decomposition will spread in the form of an explosion. If the decomposition does not produce heat or do work sufficient for its extension, then the reaction ceases.

These explosions are quite analogous to that of gunpowder, with the single exception that in the case of gunpowder the combustible constituents, charcoal and sulphur, are only mechanically mixed with the nitre, which contains the oxygen, whilst in the former the oxygen is combined chemically with the other constituents.

§ 96. **Dissociation of Gases.**—One of the simplest forms of chemical change, which is in the main produced by heat, is that which H. Sainte-Claire Deville styled dissociation. Dissociation is characterised by the decomposition lasting only so long as the cause is active, the substances returning to the original state on withdrawal of the cause. Many subtances are found to undergo dissociation; still it is often difficult to observe and demonstrate the dissociation. More especially is this the case when very high temperatures are needed to bring about the decomposition. In many instances the action is associated with a change in colour, and can be recognised by this; thus, for example, the colourless vapours of nitrogen peroxide, N_2O_4, dissociate into dark brown vapours of NO_2. Dissociation is recognisable in the increase in the number of molecules resulting from it; for, as Avogadro's law (§ 19) still holds, the density of the gas or vapour is not altered. In the case just mentioned, viz.

$$N_2O_4 = NO_2 + NO_2,$$

the number of molecules, and consequently the volume, is doubled, and therefore the density is reduced to one-half. Observations have, however, shown that this change does not occur suddenly, but takes place gradually as the temperature rises, so that, as A. Naumann has pointed out, the progress and extent of the dissociation may be calculated from the changes in volume and density.

The density of the compound NO_2 in relation to air is 1·59; therefore that of the non-dissociated compound, N_2O_4, is twice as great, viz. 3·18. Mixtures of these two, such as are produced by the dissociation, would have densities lying between these values; the more nearly the observed density approaches the lower value, the more advanced the dissociation. If in 100 particles, x have been dissociated, and therefore $100-x$ are still unaltered, then we have

$$100\ (N_2O_4) = (100-x)\ N_2O_4 + 2xNO_2.$$

Consequently there are now $100 + x$ particles instead of 100, the volume is increased in the proportion of $100 : 100 + x$, and the density, D, decreased in the inverse proportion, viz. of $100 + x : 100$. To determine x, the percentage of dissociation, we have the following proportion:

$$100+x : 100 = 3{\cdot}18 : D$$

$$x = 100 \times \frac{3{\cdot}18-D}{D}.$$

By this formula the percentage of dissociation can be calculated for every observed density; in this way the following values have been obtained:

Temperature	Density d	Dissociation x	Increase for 1° C.
		per cent.	per cent.
26·7°	2·65	19·96	0·65
35·4°	2·53	25·65	0·81
39·8°	2·46	29·23	1·10
49·6°	2·27	40·04	1·21
60·2°	2·08	52·84	1·30
70·0°	1·92	65·67	1·04
80·6°	1·80	76·71	0·88
90·0°	1·72	84·83	0·44
100·1°	1·68	89·23	0·31
111·3°	1·65	92·67	0·35
121·5°	1·62	96·23	0·18
135·0°	1·60	98·69	
154·0°	1·58	100·00	

The average increase in the dissociation for each degree centigrade rises until a maximum is reached, when the dissociation is about half completed, and then it gradually diminishes, until at 140° C. the dissociation is complete.

One might imagine that the dissociation having once begun, it must be suddenly translated through the mass so soon as the temperature required for its commencement has been reached. That this is not the case finds an explanation in the fact that in consequence of the frequent and irregular collision of the particles they do not all retain an equal velocity, and as the temperature is determined by this motion, the particles have not all the same energy. The particles having the greatest energy, *i.e.* those in the most rapid motion, are first dissociated, and those having the least heat-motion will be the last to dissociate. What we measure as the temperature of a gas is only the mean or average temperature of all the particles; some of the particles may have temperatures differing considerably from this. As great differences are seldom found, but smaller differences more frequently occur, dissociation will proceed most rapidly when the mean temperature is the same as the temperature of dissociation. At this temperature 50 per cent. of the entire mass is dissociated, and in the case of nitrogen peroxide this point is reached at 60° C.

When the temperature of dissociation is too high to permit of exact measurements of density, then, in order to make it evident, other means must be employed. Deville has employed many ingenious devices for this purpose. For instance, by diffusion through porous septa he separated the hydrogen from the oxygen formed by the dissociation of steam at a white heat, which gases, if not separated at this temperature, would recombine at a somewhat lower temperature. By rapid cooling carbon was separated from the carbon dioxide produced by the dissociation of carbon monoxide, and chlorine in a similar manner was obtained from hydrochloric acid gas.

Bunsen has shown from the pressure produced by the explosion of a mixture of two volumes of hydrogen and one volume of oxygen that combination ceases as soon as the temperature has reached about 3000° C., and therefore above this temperature steam cannot exist, but is resolved into its elements. Whether in this decomposition the molecules are resolved into atoms, thus,

$$H_2O = H + O + H,$$

or whether elementary molecules are formed,

$$2H_2O = 2H_2 + O_2,$$

has not yet been satisfactorily determined.

On the other hand, it is known that the partial decomposition of the hydrogen iodide in hydrogen and iodine takes place at 440° C., whilst the decomposition of the iodine molecules into atoms begins at 600°, and that of the hydrogen molecule, if at all, at much higher temperatures. So it is probable that the dissociation of hydrogen iodide at 400—500° C. takes place as follows :—

$$2HI = HH + II.$$

The compound is, therefore, not resolved into atoms, and the decomposition is not a case of simple dissociation, but an instance of a chemical exchange.

In the case of many liquids it has been observed that the density of their vapour is much greater at temperatures near their boiling points than at higher temperatures. Thus, according to Cahours, the density of acetic acid vapour at 250° C. is 2·08, air being the unit, which gives a molecular weight corresponding to the formula $C_2H_4O_2$. At 125° C. the density is found to be 3·2 in comparison with air. This is generally explained by assuming that at the lower temperature the vapour consists in part of particles of greater molecular weight, *e.g.* $C_4H_8O_4$, which are dissociated by further heating, as also by reduction of the pressure on the vapour.

Sulphur, aluminium chloride, and many other substances behave in a similar manner.

§ 97. **Dissociation of Liquids and of Solids.**—Liquids, both homogeneous and mixed, undergo dissociation just as gases do; but in the case of liquids it is less frequent, and also much more difficult of demonstration. Still, the colourless liquid nitrogen peroxide, N_2O_4, is observed to assume a reddish colour when warmed; showing that even in the liquid state, as is the case with the gas, it is dissociated into the red compound, having half the molecular weight and the formula NO_2. Liquids, and many solids also, are frequently dissociated when boiled. Concentrated sulphuric acid is not volatile as such, but at 325° is resolved into the anhydride and water, thus:

$$H_2SO_4 = SO_3 + H_2O$$

and these compounds on cooling re-unite with each other.

This volatilisation is not true boiling, and therefore even under reduced pressure it takes place only at the same temperature as under the atmospheric pressure (Mendeléeff). Carbonic acid, H_2CO_3, and sulphurous acid, H_2SO_3, exhibit a similar decomposition, but at much lower temperatures.

Chloral hydrate when vaporised decomposes into choral and water, thus:

$$CCl_3CO_2H_3 = CCl_3COH + H_2O,$$

and these recombine on cooling. The iodides, bromides, and chlorides of many tertiary alcohols behave in a similar manner; thus, amyl iodide yields amylene and hydriodic acid:

$$C_5H_{11}I = C_5H_{10} + HI.$$

Inorganic chlorides, bromides, and iodides exhibit dissociation, *e.g.* phosphorus pentachloride:

$$PCl_5 = PCl_3 + Cl_2.$$

Phosphorus pentafluoride is, however, volatile without decomposition.

The salts of ammonia and of substituted ammonias form a group of compounds which can only be volatilised by first undergoing dissociation (*v.* § 26). This ammonium chloride is decomposed into ammonia and hydrochloric acid: [1]

$$NH_4Cl = NH_3 + HCl,$$

and tetra-ethyl ammonium iodide is resolved into tri-ethylamine and ethyl iodide:

$$N(C_2H_5)_4I = N(C_2H_5)_3 + C_2H_5I.$$

Salts containing water of crystallisation undergo dissociation, losing their water of crytallisation partially or entirely, when the pressure of the water vapour in the atmosphere surrounding them sinks below a certain minimum. This minimum of pressure, as Andreæ has shown, varies suddenly with the proportion of water of crystallisation. For example, in the case of strontium chloride, this minimum of vapour pressure remains constant during partial dehydration so long as there is any of the salt $SrCl_2 + 6H_2O$ present, but sinks suddenly as soon as all has been converted into $SrCl_2 + 2H_2O$.

§ 98. **Dissociation in Solution.**—Dissociation may be more frequently observed in mixed liquids, in solutions, than with homogeneous fluids. The occurrence may be evidenced by a change in colour, as, for instance, when a coloured hydrated salt loses or changes its colour in consequence of a loss of water (*cf.* § 78). Thus the red compound $CoCl_2 + 6H_2O$

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[1] *V.* note to § 26, p. 41.

dissolves in water, and also in dilute spirit, forming a red solution; but on warming the solution becomes blue, either because an anhydrous compound or one containing less water is produced. On cooling the solution the red compound is again formed.

Crystallisation may in many cases be used to prove dissociation. At low temperatures from a solution of sodium sulphate, Glauber's salt, $Na_2SO_4 + 10H_2O$ separates out; whilst at 33° C. the anhydrous salt Na_2SO_4 is deposited. Many other salts behave in a similar manner.

In the case of double salts and analogous compounds dissociation may be demonstrated by diffusion, as has been shown with gaseous compounds. For example, if an open vessel filled with a solution of alum, K_2SO_4, $Al_2(SO_4)_3 + 24H_2O$, be placed in a larger vessel filled with water and allowed to remain, then, according to Graham's observations, in course of time the upper layers of water are found to contain more potassium sulphate and less aluminium sulphate than correspond to the composition of the alum. The two simple salts have, therefore, separated from each other in the solution; the double salt has been dissociated. This separation takes place because the potassium salt diffuses more rapidly than the aluminium sulphate, and therefore passes out before the other; the separation is consequently only recognised at first, as later on the inequality is compensated for. Almost all double salts behave in a similar manner, but their dissociation can only be demonstrated when the products have different rates of diffusion.

§ 99. **Electrolysis.**—Electricity offers a very powerful means of separating the dissociated products from one another. It has been known since the end of the last century that when an electric current is conducted through certain liquids the constituents are separated from one another at the points where the electricity enters and leaves the liquid. Faraday, to whom we are indebted for the investigation of the fundamental laws of this phenomenon, styled this kind of decomposition 'electrolysis'—*i.e.* analysis by electricity. Those substances capable of undergoing this species of decomposition are styled 'electrolytes,' and described as 'conductors of the second class,' conducting electricity only when simultaneously decomposed, and are distinguished in this way from (1) the 'conductors of the first class,' or 'metallic conductors,' which allow the passage of electricity without decomposition, (2) from the 'non-conductors,' or 'insulators,' which do not conduct electricity at all. The conductor of the first class, which serves to bring into and carry away the electricity from the electrolyte, is styled the 'electrode' (from ἡ ὁδός, the way). The electrode situated up-stream as regards the positive current is called the 'anode,' whilst that situated down-stream is styled the 'cathode.' Finally, the constituent passing up-stream and deposited at the anode is called the 'anion' (τὸ ἀνιόν), whilst that going down to the cathode is the 'cation' (τὸ κατιόν). Both are spoken of as the 'ions.'

For a long time electrolysis was regarded as the result of the decomposition of the electrolyte by electrical attraction, until in 1857 Clausius adduced the proof that electricity is not the cause of the decomposition, but that it can only effect the separation of the constituents of compounds already decomposed by the action of other forces. For if electricity be needed to effect the decomposition of a compound in which the constituents are held together by the force of affinity, then electrical energy in the conductor cannot produce the decomposition so long as it remain weaker than the affinity, and must, therefore, give rise to a very violent decomposition as soon as its strength somewhat exceeds this. Experience, however, shows this not to be the case, for the smallest force produces a current the intensity of which increasing in proportion to the force is sufficient to cause the 'ions' to collect together at the electrodes, or, as it is technically described, to produce the 'polarisation at the electrodes.' Since, therefore, the smallest electromotive force is sufficient to produce this effect, no expenditure of force can be needed for the decomposition of the electrolyte; this must have already taken place, the electrolyte must have been dissociated. This dissociation must have an origin similar to that spoken of in the preceding sections, and have been wrought by the rapid motion of the particles communicated as heat to the substances.

The recent investigations of Arrhenius have drawn attention to the fact that electrolytes are exactly those substances which, as already shown in § 78, produce a greater depression in the freezing point of water than is consistent with the number of their molecules in the solution, as represented by the formulæ generally accepted. Thus, whilst in the case of non-electrolytes, when their molecular weights in grams are dissolved in a litre of water, giving a so-called 'normal solution,' the freezing point of water is depressed by — 1·8° C., the haloid salts of the alkalis, for instance, give twice as great depression, for

$$NaCl - 3{\cdot}5^\circ,\ KCl - 3{\cdot}3,\ \&c.\ (v.\ \S\ 78).$$

If it be assumed that these salts are entirely or in part dissociated, in the following manner,

$$NaCl = Na + Cl,\ KCl = K + Cl$$

then the depression of the freezing point would appear to be normal; for, as there are twice as many particles present, the depression of the freezing point must be twice as great as in the case of substances which are not dissociated.

At first sight it does appear not a little remarkable that the substances which are supposed to decompose so easily should be exactly those which are formed by bodies uniting with one another with considerable energy, and to which consequently strong mutual affinities are ascribed. A further consideration shows, however, that these very same substances take part easily in chemical change of the most diverse kinds, and therefore their constituents cannot be firmly and indissolubly attached to one another. Clausius did not suppose that when, for instance, common salt is dissociated into sodium and chlorine, the individual atoms are permanently set at liberty, but rather that reunion and decomposition recur continually, each atom combining not only with the one with which it was previously united, but with any others which it may meet in the throng of atoms. This conception would appear still to be permissible; making clear, as it does, why in a solution of common salt we find neither free chlorine nor free sodium, so long as they are not brought together at the electrodes by the passage of an electric current.

§ 100. **Faraday's Law.**—According to the law discovered by Faraday, the passage of electricity from one electrode to another, through the electrolytes, takes place in such a way that for a certain amount of electricity passing through the electrolyte a given fixed quantity of each 'ion' separates out at the electrodes; so that the ions are not only equivalent to one another, but also the amount of each liberated is proportional to the quantity of electricity passing through the system. From this we must conclude that every equivalent weight of the ions can be charged by a fixed and definite amount of electricity, which it carries through the electrolyte from one electrode to the other; just as a ship takes up a given load and carries it across the ocean. The anode charged with positive electricity gives up positive, the negatively charged cathode an equivalent quantity of negative, electricity. The electrolyte takes up these charges, but in return discharges an amount of each ion equivalent to the electricity at each electrode, at the anode the electro-negative anion, *e.g.* chlorine, and at the cathode the electro-positive cation, *e.g.* sodium, is discharged.

The origin of the distinction of the ions as positive and negative is to be found in the observation mentioned in § 37, that different substances when brought in contact with one another become electrically excited, one becoming charged with positive, the other with negative electricity; and the greater the difference in the chemical characters of the substance, so much the stronger is the charge; and, further, those substances which by such contact become electro-negative in electrolysis appear as 'anions;' conversely, the electro-positive appear as 'cations.' The hypothesis has been advanced that ions united with one another in compounds are charged in like manner, and retain their charge even when dissociated. Such a supposition explains how it comes about that the positively charged anode should attract the negatively charged anion, and that the cation should be drawn to the cathode, the electrodes repelling the ions charged similarly to themselves; consequently one receives an impulse in one direction, the other in the opposite direction. When the attracted ion comes in contact with the electrode the opposing electricities neutralise one another, and the ion remains in an unelectrified state.

Now two ions, *e.g.* two chlorine atoms, which were previously charged with the same kind of electricity, and in consequence would repel one another, may combine to form a molecule of free chlorine, Cl_2, and as such appear at the anode.

By this discharge of electricity at the electrodes the liquid receives at these points an excess of the opposite electricity, that is, of the same kind as that with which the electrode is charged, and this moves with the ions through the electrolyte to the other electrode. For the transport of the electricity it is not necessary that the particles repelled by one electrode should reach the other. This movement takes place simultaneously throughout the whole of the electrolyte situated between the electrodes, the cations going always with the current, the anions against the stream; and this takes place in such a way that in every sectional area of the current there is as much electricity passing in a given time as through any other similar section, namely, as much as each electrode gives off or takes up respectively.

§ 101. **Relationship between Conductivity and Dissociation.**— As the electricity is transferred by the ions, and can only pass through the electrolyte by their aid, the undecomposed molecules taking no part in the transport, it follows that only substances capable of dissociation can act as electrolytes; and, further, they must conduct the more readily the more advanced the dissociation. In fact, Arrhenius has shown by numerous examples that all electrolytes described in § 79, whose aqueous solutions give an abnormal depression of the freezing point, are therefore partially or entirely dissociated, and that their conductivity is proportional to the extent of the dissociation as measured by the reduction of the freezing point. Those bodies, such as the chlorides of the alkali-metals, which give a reduction almost twice as great as that produced by an equal number of molecules of non-dissociable substances, are almost completely decomposed in their dilute solutions, and therefore are good conductors of electricity. In more concentrated solutions the conductivity does not increase in proportion to the amount present, but more slowly, because in such cases the dissociation is not so great. If the share in the conduction of electricity taken by each molecule be calculated by dividing the conductivity by the number of equivalent weights (expressed in grams) contained in the unit volume (1 litre), then we obtain a series of quotients which Kohlrausch has styled the specific molecular conductivity;[1] and this increases with increased dilution, and therefore with increasing dissociation. The conclusions arrived at in § 79 find a most satisfactory confirmation in this behaviour of electrolytes.

The knowledge of the interdependence of dissociation and electrolytic conductivity enables one to explain the statement made by F. Kohlrausch that at the ordinary temperature only mixtures conduct electricity, the several constituents of which are, however, non-conductors. Thus, whilst a mixture of water and hydrochloric acid gas is a good conductor of electricity, because the hydrochloric acid gas is almost completely dissociated, still neither pure water nor liquefied hydrochloric acid gas is a conductor. At a red heat, when the tendency to decomposition is greater, many homogeneous substances are electrolytes.

§ 102. **Migration of the Ions.**—As the positive electricity is alone transported by the cations, and the negative by the anions, and as exactly equal amounts of each are simultaneously deposited at both electrodes, one might be inclined to think that what holds true for the different kinds of electricity will also apply to the ions, and that equal quantities of each ion must pass simultaneously through any section of the current. This is, as Hittorf has shown, not the case; nor is it necessary that it should be, for as far as the transport of electricity is concerned, it is immaterial whether a number of positive ions move to one side or an equal number of negative ions pass to the other side. A deficiency of one kind may therefore be compensated by an excess of another. The transference of electricity, however, is proportional to the sum of the quantities of both the ions deposited; the electrolytic conductivity is also proportional to this amount, which consequently may be used as a measure of the conductivity.

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[1] Strictly speaking, the addition 'molecular' is not correct, as the specific conductivity is given in terms, not of molecular, but of equivalent weights.

The ratio of the velocities of the anions and cations may also be determined. It is only necessary, after the electrolysis has gone on for a little time, to determine, by an analysis of those portions of the liquid surrounding the electrodes, what quantities of each ion have passed through the central and still unaltered portion of the liquid. Hittorf has made a large series of such determinations, and found that the migration of the ions, as he styles it, takes place with very unequal velocities. If the anion and cation were to move at equal rates, then for every single equivalent weight of each deposited at the electrodes one half of this amount of each must during this time pass through the intermediate layers of the electrolyte; for by the complete symmetry of the operation one half of the positive electricity released at the cathode is provided by the positive ions, coming from the side of the anode; the other half is thus free, so that the negative ions may pass from the cathodes towards the anode. This, according to Hittorf's investigations, happens in some cases, for example, in a moderately dilute solution of potassium chloride, in which for every equivalent of potassium, $K=39{\cdot}03$, deposited at the cathode, and every equivalent of chlorine, $Cl=35{\cdot}37$, deposited at the anode, and giving up their charge of electricity, the half of each of these quantities passes from one half of the solution to the other. If now we take the case in which, for instance, the cation of an electrolyte is entirely or almost completely immovable, electrolytic conduction and decomposition may still take place; in such a case, however, the transport of electricity is effected by the anion entirely, of which, therefore, an entire equivalent must pass from the side of the cathode to the anode, so that a loss of anion takes place in the portion of the liquid surrounding the cathode, and the loss in that portion surrounding the anode produced by the deposition of the anion is completely compensated for by this migration. Moreover, as one equivalent of the cation is deposited at the cathode, it is evident that the entire expenditure is borne by that portion of the electrolyte surrounding the cathode. At this point the liquid must become very much diluted, whilst in other parts the concentration will remain unaltered. Such an extreme case has certainly never been observed; but all instances hitherto investigated lie between this and the first case considered.

The number expressing the fraction of an equivalent of an ion transferred from one electrode to the other in the time during which an equivalent of each is liberated at the electrodes Hittorf has styled the 'transport number,' and represents it by '*n*.' For example, from a solution of one part of crystallised copper sulphate, $CuSO_4 + 5H_2O$, whilst 0·2955 gram of copper is deposited on the cathode, 0·0843 gram only passes through the intermediate and unaltered layers of the liquid from the side of the anode to the cathode. In this instance, then, we have n for copper equal to 0·285.

$$\frac{0·0843}{0·2955} = 0·285.$$

Instead of half an equivalent of the metal passing through the unaltered section of the current, little more than a quarter passes. This portion of the electrolyte does not contain the free ions but simply the neutral salt, proving that the ions exist in equivalent proportions; it therefore follows that the quantity of the anion passing against the current has proportionately increased—in fact, 0·715 equivalent of SO_4, thus:

$$1 - n = 1 - 0·285 = 0·715 \text{ equivalent } SO_4.$$

The sum of the transport numbers of the two ions is always equal to unity. They are almost invariable, but in some cases alter somewhat with the concentration.

For instance, in the case of potassium bromide, the 'transport number' for bromine changes. For a solution of 1 part of the salt in 2·36 parts of water it is 0·493, in 116·5 parts of water it is 0·546. The transport number of the potassium falls in a corresponding manner from 0·507 to 0·454. In the more dilute solutions the velocity of the bromine compared to that of the potassium is somewhat increased.

§ 103. **Velocities of the Ions.**—By the aid of the transport numbers and the determinations of the conductivity of solutions, F. Kohlrausch has calculated the velocities of the single ions. The electrical conductivity of a body depends not only on its material composition, but also on its dimensions and the temperature. According to Ohm's law it is proportional to the sectional area, and inversely proportional to the length of the conductor; in electrolytic conduction it rises with increased temperature, but decreases with rise in temperature in case of metallic conduction. By maintaining the temperature and dimensions constant—in other words, by comparing conductors of exactly the same form at the same temperature, and in the case of liquids using vessels of exactly the same width and length—results are obtained which enable us to fix the relation between the conductivity of the electrolyte and the quality and quantity of its constituents.

As pure water does not conduct, the conducting power of an aqueous solution depends chiefly upon the nature and amount of the substance dissolved in it, and in fact is determined, not by the total amount dissolved, but only by the portion dissociated (*cf.* § 101). If the specific molecular conductivity of such a solution be calculated, a number is obtained which is dependent not only on the number of molecules dissolved but also upon the extent of their dissociation. Since this dissociation is complete only when the dilution is infinitely great, only such diluted solutions should be used for comparison, which is by no means easily done. These difficulties may be avoided by comparing solutions which contain in a given volume an equal number of molecules in a similar state of dissociation. If this be at least approximately the case, and both contain an equal number of ions in a given volume, the differences in the specific conductivity can only be due to the difference in the mobility of the ions, and may, therefore, serve for its determination.

The specific conductivity λ can be represented as the sum of two values, one u proportional to the velocity of the cation, the other v proportional to that of the anion; thus

$$\lambda = u + v.$$

But as the proportion of both these parts is given by the transport numbers, we have

$$u : v :: 1 - n : n$$

n representing the transport number of the anion. Two equations are thus obtained for the determination of the unknown u and v, viz.

$$u = (1 - n)\,\lambda, \quad v = n\,.\,\lambda.$$

Calculating by the aid of this expression the velocity of one and the same ion from the conductivity of its different compounds, satisfactory results are obtained, as Kohlrausch has shown, so long as salts of monobasic acids only are compared with one another. The following table contains the velocities of ions calculated by Kohlrausch and expressed in terms of an arbitrary standard, in which λ is measured in terms of the ten-millionth part of the conductivity of mercury, or the latter is set down as 10^7.

Cations	$u.\,10^7$	Anions	$v.\,10^7$
H = 1	272	OH = 16·96	143
Li = 7	24	F = 19·06	30
Na = 23·0	32	Cl = 35·37	54
K = 39·0	52	Br = 79·76	53
NH_4 = 18·01	50	I = 126·54	55
Ag = 107·66	42	CN = 25·98	50
$\frac{1}{2}$ Mg = 12·15	26	NO_3 = 61·89	48
$\frac{1}{2}$ Ca = 19·95	26	ClO_3 = 83·25	42
$\frac{1}{2}$ Sr = 43·65	28	$C_2H_3O_2$ = 58·86	26
$\frac{1}{2}$ Ba = 68·45	30		
$\frac{1}{2}$ Cu = 31·59	29		
$\frac{1}{2}$ Zn = 32·55	24		

If these velocities are expressed in absolute terms, it is then seen that they are very small even under the influence of a strong electromotive force, and the particles move in a second through a few hundredths or a tenth of a millimetre, and consequently at a snail-like speed. It is evident that they meet with considerable opposition to their movement.

§ 104. **Relation between Electrolytic Conduction and Diffusion.**—The intimate relationship between electrolytic conduction and the motion of the particles is shown also in the fact that those movements which take place independently of electricity vary in a similar manner. J. H. Long has proved experimentally that the velocities with which different salts of analogous composition diffuse into water stand to one another in approximately the same relation as their electrolytic conductivities, so that the compounds which diffuse the most easily are the best conductors. This statement is not absolutely true, but holds only for certain groups of compounds of similar composition, because in different groups the extent of the dissociation is different, and undecomposed molecules diffuse with velocities other than those of the ions.

That many salts are in reality resolved into their ions and do not, or only in part, diffuse undecomposed, is also shown by Long's observations; for the comparison of compounds containing the same anion—for example, the chlorides—has shown that the rate of diffusion is inversely proportional to the transport number of the anion; but the comparison of salts with the same cation—for example, the potassium salts—has demonstrated the rate of diffusion to be directly proportional to the transport number of the anion. This practically amounts to saying that, if two salts have the same ion in common, then the salt with the more mobile second ion is the more easily diffusible. The rate of diffusion would therefore appear to be the sum of the velocities of the ions.

§ 105. **The Function of the Ions in the Production of Electric Currents.**—The close relationship between the electrolytic ions and the movement of electricity is seen also in the fact that electric currents are produced by the contact of unequally concentrated solutions of electrolytes simultaneously with the diffusion tending to compensate for the inequality in concentration. The intensity of the currents can be shown, both experimentally and theoretically, to be related to the velocities of the ions.

The electric currents produced ordinarily by contact of two or more metals with one another or with one or more electrolytes appear to owe their origin to the free and mobile ions set at liberty by dissociation. The chemical affinity of the metals for the anions exercises an attraction on these. By the deposition of the anions on the metal and the giving up of their negative electricity the metal becomes so charged with electricity that the further approximation of the anions is prevented. The strength of this charge of negative electricity is greater the greater the affinity of the metal for the anion. For instance, if two metals, like copper and zinc, are immersed in a liquid, then the metal, in this case zinc, possessing the stronger affinity will be charged more strongly with negative electricity than the other, viz. the copper. If the two metals are united by a metallic conductor, then the more strongly charged zinc will give up its negative electricity to the copper, and in return receive a charge of positive from the copper. Thus the equilibrium at the points of contact of the two metals and the electrolyte is disturbed; in consequence of the reduced negative charge of the zinc, more anion is attracted, and the increased negative charge of the copper induces a repulsion of the anion, and cations are attracted by reason of their positive charge. In addition, at the point of contact of both metals there is a separation of electricity opposite to the charge produced by the ions. Equilibrium cannot be established so long as both the metals are in contact with each other and the electrolyte. But as the ions collect more and more on the metals and cover them, the negative anion on one, and the positive cation on the other, the ions take the place of the metal and thus reverse the action completely; for the positive cation attracts the anion, and the reverse. This separation of the ions which produces a current opposed to the original is styled 'electric polarisation.'

In order, therefore, to produce a constant current the separation of the ions at the electrodes must be prevented, or in other ways made innocuous, which end can be attained by suitable choice of the electrolyte. In this way constant electric batteries can be produced. Daniell's battery is one of the oldest of this kind, and consists of a plate of copper surrounded by a solution of copper sulphate, $CuSO_4$, and a plate of zinc immersed in dilute sulphuric acid, and separated from the copper by a porous cell. The zinc attracts to itself the anion, SO_4, and repels the cation, H_2, and is charged with negative electricity, which passes over to the copper on which the positive cation, Cu, collects; whilst if the copper and zinc were not in contact the copper would also be surrounded with the anion, SO_4. The precipitate of copper on the copper plate leaves the latter unchanged; the zinc remains unaltered, because by combining with the anion, SO_4, zinc sulphate, $ZnSO_4$, is formed which dissolves in the water.

The combination remains, therefore, almost entirely unchanged so long as zinc, acid, and copper sulphate are present.

According to the conception, put forth recently by L. Sohncke, and developed uniformly by the use of the older representations, the source of the electric current, respecting which there has been so much discussion, is to be sought neither in the contact of the metals nor in the chemical action of the metals, but in the dissociated state of one or other of the electrolytes in contact with the metals. This completely confirms the observation made by F. Kohlrausch, that simple unmixed liquids are not as a rule electrolytes, and are therefore incapable of developing a current unless in the fused state and at high temperatures. Dissociation produced either by mixing with other liquids or by the application of heat is therefore essential to the action of electrolytes.

That in aqueous solutions hydrogen chloride exists to a large extent in a state of dissociation (*cf.* § 109) can be demonstrated by the depression of the freezing point (*cf.* § 78). Still, the mode of dissociation cannot in this case be determined ; for by the electrolysis of concentrated solutions hydrogen and chlorine are the ions, whilst from dilute solutions hydrogen and oxygen are formed. Hence it would appear probable that in the first case the hydrogen chloride is decomposed into hydrogen and chlorine, and in the second case the solution contains the compound $HCl + H_2O$, or H_3ClO, the existence of which Thomsen assumes, and this is resolved into H_2 and $HClO$, the latter yielding oxygen, O, and hydrochloric acid, HCl, at the anode.

§ 106. **Dissociation a Condition Preparatory to Chemical Change.**—In the majority of cases it would appear that dissociation must precede chemical change ; for the electrolytes which are so easily dissociated belong to the class of substances distinguished by their ability to take part in chemical actions. This ability ceases so soon as the possibility of this dissociation taking place is removed. Anhydrous hydrogen chloride, liquefied by pressure and cold, does not attack the metals, which are easily dissolved by its aqueous solutions.

This extremely interesting and remarkable phenomenon becomes perfectly clear in the light of the hypothesis that pure hydrogen chloride cannot be dissociated and remain so, because each of the separated ions must come in contact with others and be fixed by these, whilst in the aqueous solutions they would both be separated by the water, and remain apart for a short time.

The behaviour of many elements is very remarkable according as they exist in compounds which are electrolytes or non-conductors, *i.e.* in compounds which do not undergo dissociation. Thus, for instance, chlorine, bromine, and iodine are separated from their compounds by solutions of silver salts only when the compounds are such as easily dissociate, and these elements form the ions. The majority of organic compounds containing these halogens are either incapable of being dissociated or dissociate at high temperatures only, and then only in some cases is the dissociation such that the halogens chlorine, bromine, and iodine appear as ions. In complete agreement with these facts, the chlorine, bromine, and iodine of such compounds either do not react at all with silver nitrate or only slightly ; many other compounds of these and other elements behave in a similar manner. The chlorine of chlorates and perchlorates in which the metals are the cations and the radicals ClO_3 and ClO_4 the anions, does not in solution give any silver chloride, but forms first silver chlorate and perchlorate, from which the chloride can be produced by their decomposition. The sulphates with the anion SO_4 in the ordinary course of things give rise to sulphates with the same 'anion,' and many other salts and similar compounds behave in the same way. The compounds may decompose in other ways if the manner of the dissociation, and consequently the nature of the ions, be changed by heat or by the action of other bodies.

If by the study of a series of compounds capable of undergoing dissociation the ions contained in them are known with any degree of certainty, the majority of the reactions of these compounds may be predicted, for the combinations and changes always result from the union of the ions with those of the other active bodies. These facts afford an explanation of the principle known as the ‘conservation of the type’—a rule which has been recognised for a considerable length of time, and which states that the bodies produced in any given reaction belong to the same types as those from which they are formed; in other words, they represent compounds analogous to those from which they are produced. An acid and a salt yield usually by their mutual reaction a salt and an acid, thus:

$$\mathrm{H} \vdots \mathrm{Cl} + \mathrm{Ag} \vdots \mathrm{NO_3} = \mathrm{Ag} \vdots \mathrm{Cl} + \mathrm{H} \vdots \mathrm{NO_3}.$$

A sulphate and a nitrate act upon one another to form by exchange of metals another sulphate and nitrate:

$$\mathrm{K_2} \vdots \mathrm{SO_4} + \mathrm{Ba} \vdots \mathrm{2NO_3} = \mathrm{Ba} \vdots \mathrm{SO_4} + \mathrm{2K} \vdots \mathrm{NO_3}.$$

Again, a hydroxide and a salt form another salt and hydroxide:

$$\mathrm{Ba} \vdots \mathrm{(OH)_2} + \mathrm{Mg} \vdots \mathrm{(NO_3)_2} = \mathrm{Mg} \vdots \mathrm{(OH)_2} + \mathrm{Ba} \vdots \mathrm{2NO_3},$$

and so on. Changes of this kind take place in all probability even when the final result is different from what this rule would lead one to expect; the instability of one or other of the compounds formed may lead to the formation of new substances. Thus cupric iodide should be formed by the action of potassium iodide on copper sulphate:

$$\mathrm{2K} \vdots \mathrm{I} + \mathrm{Cu} \vdots \mathrm{SO_4} = \mathrm{K_2} \vdots \mathrm{SO_4} + \mathrm{Cu} \vdots \mathrm{I_2}.$$

But cuprous iodide and iodine are formed by reason of the instability of cupric iodide:

$$\mathrm{2Cu} \vdots \mathrm{I_2} = \mathrm{Cu_2} \vdots \mathrm{I_2} + \mathrm{I_2}.$$

The action of potassium hydroxide on silver nitrate affords another example of a similar kind; the product should be silver hydroxide and potassium nitrate:

$$\mathrm{K} \vdots \mathrm{OH} + \mathrm{Ag} \vdots \mathrm{NO_3} = \mathrm{K} \vdots \mathrm{NO_3} + \mathrm{Ag} \vdots \mathrm{OH},$$

but the silver hydroxide decomposes into silver oxide and water, thus:

$$\mathrm{2Ag} \vdots \mathrm{OH} = \mathrm{Ag_2} \vdots \mathrm{O} + \mathrm{HOH}.$$

Numerous other examples might be given in which the ‘type’ is not maintained.

For the commencement of the reaction it would appear to be sufficient if one of the reacting substances is capable of dissociation, although the other is entirely incapable of being dissociated. Thus benzene and many other hydrocarbons do not undergo dissociation at the ordinary temperature; yet when brought in contact with bodies which easily dissociate, the ions energetically attack the hydrocarbon. With chlorine the following change takes place:

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Chlorine}}{Cl \vdots Cl} = \underset{\text{Chlorobenzene}}{C_6H_5Cl} + \underset{\text{Hydrochloric acid}}{HCl}$$

The reaction takes place more readily if the unstable iodine chloride is substituted for chlorine.

Somewhat similar but more complex is the nitration of benzene, which is probably not effected by the ordinary ions. Dilute nitric acid does not attack cold benzene, but the strong acid does. It readily decomposes into the anhydride and water, $2HONO_2 = HOH + N_2O_5$. The anhydride and benzene interact.

$$\underset{\text{Anhydride}}{NO_2 \vdots ONO_2} + \underset{\text{Benzene}}{C_6H_6} = \underset{\text{Nitrobenzene}}{NO_2C_6H_5} + \underset{\text{Acid}}{HONO_2}$$

The nitration ceases long before all the nitric acid is consumed. which is evidence in support of the accuracy of the above equation. When neither of the substances dissociates, then, as a rule, no reaction takes place, or a rise in temperature is needed to start the reaction, which aids or simply induces dissociation.

Free oxygen, O_2, does not appear to be easily dissociated, for the oxidation of most bodies by its aid can only be effected at high temperatures. It is, however, dissociated by electricity, and ozone produced, which probably has the formula O_3. Ozone is extremely easily dissociated, and, as is well known, acts as a powerful oxidising agent.

It is very remarkable that many substances, such as phosphorus, are less easily oxidised by pure oxygen than by air, in which the oxygen is diluted with a considerable proportion of nitrogen, or even by oxygen rarefied by reduction of pressure. Since phosphorus when slowly oxidised is luminous in the dark, these facts may be readily observed.

In pure oxygen at 20° C. and under a pressure of 760 mm. no light is given out; the phosphorus becomes gradually luminous as the pressure is reduced, and is very distinctly so when the pressure has fallen to 150 mm., or to about $\frac{1}{5}$ of an atmosphere. This remarkable phenomenon is probably in part due to the fact that the dissociation of the oxygen particles is favoured by the attenuation.

§ 107. **Rates of Chemical Change.**—Every chemical action requires a certain length of time for its completion. The time required is, however, very different, varying with the nature of the reacting substances, their amounts, and the conditions under which they are brought together. Hitherto this subject has been thoroughly investigated only in comparatively few cases. In most instances the conditions are so complex that it is difficult to separate and estimate their various influences. Numerous observations show, however, that the rapidity of a chemical action is influenced by the quality, the quantity and the mass of the reacting bodies; also by their state of aggregation, as well as that of the products; further, by temperature and pressure, and by the presence of bodies taking no active part in the action, such as solvents and diluents, &c. The influence of mass, solubility, and volatility was submitted to a thorough examination by Claude Louis Berthollet more than a hundred years ago; but only in recent years have his endeavours obtained their just recognition, and the work been resumed and extended by the aid of more modern methods.

§ 108. **Simple Decomposition.**—The simplest case is that in which, with several active substances present, one only of these undergoes a change. Such a case we have in the inversion of cane sugar under the influence of a dilute acid,[1] whereby it is converted into a mixture of dextrose (grape sugar) and lævulose (fruit sugar), which rotates the plane of polarised light in the opposite direction to that in which it is rotated by cane-sugar solutions. This decomposition, represented by the equation

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[1] We may neglect the part played by the water in this reaction, as also that of the acid, the proportion of which remains unchanged.

$C_{12}H_{22}O_{11}$	+	H_2O	=	$C_6H_{12}O_6$	+	$C_6H_{12}O_6$
Cane sugar				**Grape sugar**		**Fruit sugar**

has been carefully investigated by Wilhelmy, and more recently by Ostwald. If a given quantity of sugar dissolved in water be mixed with a definite amount of an acid, capable of producing the inversion, then in every interval of time an amount of the sugar is inverted which is proportional to the amount of sugar still remaining unchanged. If A be the quantity of sugar originally present, and x the quantity of sugar inverted during the time, t, which has elapsed since mixing, then the amount dx inverted in the infinitely short interval of time dt is proportional to the amount $(A - x)$ remaining unaltered. In this manner we obtain the differential equation:

$$\frac{dx}{dt} = K.(A - x), \quad \frac{dx}{A - x} = K.dt$$

in which K represents a constant, or in this case at least an invariable quantity. By integration the following expression is obtained for the amount x inverted in the time t

$$-\log_e (A - x) = K.t + \text{constant}.$$

Reckoning t from the moment of mixing, when $t = o$, x also $= o$; consequently the integration constant is

$$-\log_e A = \text{const}.$$

and $$\log._e \frac{A}{(A - x)} = K.t$$

and from these we have

$$\frac{A}{A - x} = e^{K.t}$$

$$x = A\left(1 - \frac{1}{e^{Kt}}\right) = (1 - e^{-K.t})$$

in which e represents the base of natural system of logarithms, viz. $e = 2{\cdot}71828$.

The general correctness of these equations has been verified and the quantity $\log_e \frac{A}{A - x}$ may be calculated from the value of x, determined experimentally, and divided by the corresponding values of t. The values of

$$K = \frac{1}{t} \cdot \log_e \frac{A}{A - x}$$

have thus been found to be constant, as is required by theory. The quantity of sugar, therefore, inverted every moment is proportional to the amount of unaltered sugar present; and of this equal portions are always inverted in equal times.

The invariable quantity K is not absolutely constant, but varies with the nature as well as with the amount of the acid used for inversion, and also with the proportion of sugar contained in a given volume of the solution, consequently with the concentration of the solution. An alteration in the mass of the acid is of much greater influence than a change in the quantity of the sugar. According to Ostwald's experiments, by increasing the sugar to ten times the amount whilst the hydrochloric acid remains constant, the value of K is only increased by half its original value. The increase in the proportion of acid, with the sugar remaining constant, produces a different effect, according to whether the acid is strong and easily dissociated, or weak and one which does not easily dissociate.

With the strong acids, such as nitric, hydrochloric, and hydrobromic acids, the inversion is approximately proportional to the amount of the acid, but decreases with the dilution to a somewhat greater extent than would correspond to the amount of the dilution. In the case of the weaker organic acids—formic, acetic, propionic, butyric, and succinic acids—the inversion takes place more slowly than the increase in the dilution warrants; so that without doubt the more dilute acids have a stronger action, because they are more completely dissociated.

Many other reactions take place in accordance with Wilhelmy's formula, the amount decomposed at each interval of time being proportional to that which still remains unaltered. This, according to Harcourt and Esson, is the case in the reduction of permanganic acid by a large excess of oxalic acid, and also in the reduction of hydrogen peroxide by hydriodic acid. According to Ostwald, the so-called saponification of ethereal salts soluble in water, such as methyl acetate by dilute acids, follows this law also; this reaction is no doubt analogous to the inversion of sugar, for the ethereal salt by the assimilation of water is resolved into alcohol and acid. According to Van't Hoff the replacement of chlorine or bromine in organic compounds by hydroxyl (OH) with or without subsequent splitting off of water affords another instance to which this logarithmic formula may be applied; many other reactions also might be cited.

§ 109. **Double Decomposition.**—The case is somewhat less simple when two substances are simultaneously changed. Strictly speaking, this is the case in some of the reactions discussed in the foregoing section, inasmuch as water takes part in the change. Its influence is not perceived, because, for example, in the inversion of sugar the amount of water assimilated scarcely alters the large excess of water present. Similarly, in the reduction of permanganic acid and of hydrogen peroxide by so large an excess of the reducing agent, the changes in the amounts of these do not come into consideration.

If in any reaction the two active substances are in solution, their masses are then most conveniently calculated in equivalent weights, *i.e.* according to the number of these proportions which react with one another. If A be the number of equivalents of one substance, and B that of the other, and x the number of equivalents of each decomposed in the time t, then, assuming the change is always proportional to the reacting mass, the reaction would be represented by the following differential equation:

$$\frac{dx}{dt} = \mathrm{K}\,(\mathrm{A} - x)\,(\mathrm{B} - x)\,;\quad \frac{dx}{(\mathrm{A} - x)\,(\mathrm{B} - x)} = \mathrm{K}\,.\,dt.$$

For equivalent amounts of both substances, that is, when A=B, the equation assumes the form

$$\frac{dx}{(\mathrm{A}-x)^2} = \mathrm{K}\,.\,dt\,;$$

and when integrated, with $t = o$ and $x = o$, the following expression is obtained:

$$\frac{x}{A-x} = A \, . \, K \, . \, t.$$

According to this expression the relation of the amount of the decomposed to the amount of the unaltered substances is variable with and proportional to the time. For a long time no single case has been observed which corresponded to this rule, until it was shown by Hood to apply in the oxidation of ferrous sulphate by chloric acid. The amounts of these substances equivalent to one another in this case are $1HClO_3$ and $6FeSO_4$. Instead of using these substances, $1KClO_3$ and $6FeSO_4$ were mixed together with dilute sulphuric acid, and the proportion of unoxidised iron was determined by the titration from time to time of a sample taken from the mixture. The results are in accord with the above equation. It has also been shown by R. Warder that the saponification of ethyl acetate by an aqueous solution of caustic soda proceeds in a manner confirmatory of this law; and Van't Hoff and Schwab have shown the same to be the case with the conversion by caustic soda of monochloracetic acid into glycollic acid; and according to Ostwald the decomposition of acetamide by dilute acids into ammonium salts and acetic acid proceeds in a similar manner.

If A and B are different the integration of the above equation yields the following expression:

$$\log_e \frac{B\,(A-x)}{A\,(B-x)} = (A-B) \, . \, K \, . \, t;$$

or by introducing the proportion of A to B

$$A : B = 1 : n$$

we obtain

$$\log_e \frac{A - \frac{x}{n}}{A - x} = A\,(n-1) \, . \, K \, . \, t.$$

This equation has also been confirmed by a certain number of observations.

It must, however, be confessed that the number of quantitative observations hitherto made to test the theory is altogether out of proportion to the innumerable chemical investigations undertaken in this century, despite the desirability and necessity for such observations.

§ 110. **Reversible Reactions.**—Remarkable relationships are observed when the products of a reaction so react upon one another as to form again the original substances, and thus reproduce the condition from which they started. This is the case when two or more electrolytes in solution react, and their ions combine in such a way as to produce all the several possible combinations. The simplest of all such cases is that when the substances produced by the combination of the ions are neither insoluble in the solvent used, nor volatile, and consequently neither separate out in the solid nor in the gaseous state. When this possibility is excluded, and all remain in solution, the reaction then proceeds according to the law discovered by Guldberg and Waage, which is but the corrected form of the law proposed about a century ago by C. L. Berthollet. This is usually described as the 'Law of the Action of Mass.'

This law comes into play when, for instance, an acid is brought into a solution of another salt; when alcohol is added to an acid or an ethereal salt treated with water. In the first case the free acid decomposes a portion of the salt, so that the solution contains both the free acids and salts of each of them. For instance, if hydrochloric acid be added to a not too concentrated solution of nitre the solution will contain not only unaltered potassium nitrate, but also potassium chloride, free nitric and free hydrochloric acids. In fact, for the ultimate division of the constituents it does not matter whether the nitrate has been treated with hydrochloric acid or the chloride with nitric acid, provided only that in both cases the proportions of all substances concerned are the same.

In the second instance the acid and alcohol produce an ethereal salt and water, which in turn give rise to the alcohol and acid; and here, also, if sufficient time elapses, the final condition in which all four substances are present is the same, whether we start with one or the other set of combinations. If, for example, acetic acid and alcohol are mixed in the proportion of their molecular weights, then, according to Berthelot and Pean de St. Gilles, they react upon one another in accordance with the following equation:

$$\underset{\text{Acetic acid}}{(C_2H_3O)\,OH} + \underset{\text{Alcohol}}{(C_2H_5)OH} = \underset{\text{Ethyl acetate}}{(C_2H_3O)\,O\,(C_2H_5)} + \underset{\text{Water}}{HOH}$$

forming ethyl acetate and water until two-thirds of the whole mass is decomposed in this manner. On the other hand, when the ester and water are mixed in molecular proportions, the reverse reaction proceeds until one-third is converted into alcohol and acid. Consequently, in the final condition, whether this be reached from one side or the other, the mixture contains one molecular proportion of alcohol and of acid for every two molecular proportions of ester and of water, so that the condition of equilibrium in the mixture is represented as follows:

$$(C_2H_3O)\,OH + (C_2H_5)\,OH + 2(C_2H_3O)\,O\,(C_2H_5) + 2HOH.$$

This condition of equilibrium is not to be looked upon as a state of rest, in which, when once reached, no further reaction takes place, but is to be regarded rather as a state in which just as many particles react in one way as there are particles reacting in the opposite, the two opposing reactions maintaining the equilibrium.

A simple consideration shows that the frequency of either of these reactions increases with the number of interacting particles present. Since the particles must come in contact with each other in order that they may combine or react, it is apparent that the space in which they are confined must be of influence; for, indeed, generally speaking, the reaction will be the more complete the larger the number of particles contained in a given space in the unit of volume. Yet, again, it is to be remembered that every particle present is not to be looked upon as taking part in the action. The number of such active particles present is dependent upon the degree of dissociation, which, as has been already shown, usually changes with the dilution of a solution, and, as a rule, the extent of the dissociation increases with the increase of the dilution. If, however, the dissociation, and consequently the chemical activity, be so far advanced that any further alteration in the concentration no longer exercises any great influence, the change is then almost proportional to the masses of the active bodies present in the unit volume—for example, in a litre.

Guldberg and Waage's theory of the action of mass is based upon this assumption, the truth of which has been confirmed by numerous observations.

§ 111. **Guldberg and Waage's Theory of the Action of Mass.** Let A and B′ represent two bodies which interact according to the equation

$$A + B' = A' + B;$$

and let the reaction be reversible,

$$A' + B = A + B';$$

then, if the two bodies A and B′ are brought together, both reactions will go on concurrently until a state of equilibrium ensues, in which the two opposite reactions take place to the same extent.

Let p, q, p', and q' denote the number of particles which are present in this state; then

$$p \,.\, A + p' \,.\, A' + q \,.\, B + q' \,.\, B'$$

will represent the composition of the mixture in the state of equilibrium. Assuming that the action is proportional to the mass, the change represented by the first equation is proportional to the number of particles A and B′, and is consequently proportional to the product $p \,.\, q'$, and the reverse reaction represented by the second equation is proportional to $p' \,.\, q$. The action in the unit of time is expressed by the formulæ $K \,.\, p \,.\, q'$ and $K' \,.\, p' \,.\, q$; K and K′ being factors which depend on the nature of the bodies and on external conditions such as temperature, but they remain constant so long as these conditions are unchanged. The state of equilibrium in which the reaction takes place to the same extent in one direction as it does in the reverse is represented by the equation

$$K \,.\, p \,.\, q' = K' \,.\, p' \,.\, q;$$

or
$$\frac{p'}{p}=\frac{K}{K'}\cdot\frac{q'}{q}=\chi^2\frac{q'}{q},$$

in which $\frac{K}{K'}$ is replaced by the symbol χ^2. If the values $\frac{p'}{p}$ and $\frac{q'}{q}$ are termed *quotients of decomposition*, then the law may be expressed in the following words: In the state of equilibrium the quotients of decomposition bear a fixed relation to each other.

For example, let A and B be acids and A′ and B′ salts of these acids; then the quotients of decomposition indicate for each acid the ratio the non-neutralised bears to the amount of neutralised acid. When the constant χ^2 is once determined this ratio can be calculated for any given case.

§ 112. **Experimental Proof of Guldberg and Waage's Law by Etherification.**—Different methods have been proposed for determining the constant of affinity, χ^2. It can be easily determined in the process of the formation of an ethereal salt or ester from an acid and alcohol. If R is an alcoholic radical and S an acid radical, the formation of an ethereal salt is represented by the equation

$$ROH+SOH=ROS+HOH,$$

and the state of equilibrium by

$$p\,ROH+q'\,SOH+p'\,ROS+q\,HOH;$$

$$\frac{p'}{p}=\chi^2\frac{q'}{q}.$$

If P molecular weights of alcohol and Q molecular weights of acid are used, and the amount of free acid q' in the state of equilibrium is determined by titration, then χ^2 and the coefficients p, p', and q can be determined by means of the following equation:

$$P=p+p'; \qquad Q=q+q'; \qquad \chi^2=\frac{p'\cdot q}{p\cdot q'}.$$

If only acid and alcohol are mixed together without the addition of ethereal salt or water, then the quantities of the latter are equivalent to each other and $p'=q$:

For the sake of simplicity let $P=Q=1$; then

$$p=1-p'=1-q=q'; \qquad \chi^2=\left(\frac{1-q'}{q'}\right)^2.$$

In this case if $R=C_2H_5$ and $S=C_2H_3O$ the result of experiment for acetic acid and ethyl alcohol is that $q'=\frac{1}{3}$.

It therefore follows that $\chi^2=4$ and the state of equilibrium is represented by $1ROH+1SOH+2ROS+2HOH$. That is to say, if we take equivalent quantities of alcohol and acetic acid, two-thirds will interact to form ethyl acetate and water and one-third will remain unaltered.

After determining the value of χ^2 in this way, the validity of the theory can be tested by taking any other values for P and Q and determining the quantity q' of free acid and comparing the experimental result with the value calculated by means of the factor $\chi^2=4$. The agreement between the experimental and calculated results has been found to be most satisfactory, even when certain quantities of water and ethereal salt were added, provided that the water was not added in sufficient quantity to cause the liquid to separate out into two layers.

In this case the value of χ^2 is not greatly influenced by temperature, and it varies within rather narrow limits for different organic acids and alcohols, possessing analogous atomic linking. According to Menschutkin, in the case of the action of the fatty acids, $C_nH_{2n}O_2$, on isobutyl alcohol, χ^2 increases with the molecular weight of the acid; $\chi^2=3{\cdot}2$ when $n=1$ (formic acid) and $\chi^2=5{\cdot}9$ when $n=8$ (caprylic acid). In spite of this rather large difference in the constants, the difference in the quantity of undecomposed acids is not very large.

For instance, when $P=Q=1$ the following results are obtained:

		$q'=p$	$q=p'$	χ^2	χ
Formic acid[1] .	$C_1H_2O_2$	0·358	0·642	3·22	1·79
Acetic acid . .	$C_2H_4O_2$	0·326	0·674	4·28	2·07
Propionic acid .	$C_3H_6O_2$	0·313	0·687	4·82	2·20

[1] At 100° C., the other acids at 154°

		$q^1 = p$	$q = p^1$	χ^2	χ
Butyric acid . .	$C_4H_8O_2$	0·305	0·695	5·19	2·28
Caproic acid . .	$C_6H_{12}O_2$	0·302	0·698	5·34	2·31
Caprylic acid .	$C_8H_{16}O_2$	0·291	0·709	5·94	2·44

The state of the equilibrium is slightly different for different acids: this is shown under χ in the preceding table, which contains the number of equivalents of acid etherified for each equivalent of unaltered acid (assuming that the acid and alcohol were present in equivalent quantities).

§ 113. **Avidity of Acids.**—Julius Thomsen and W. Ostwald have investigated the changes which take place when two acids act upon one base, which is not present in sufficient quantity to neutralise them both, or when two bases act on one acid under similar conditions. The constant χ which determines the ratio between the amounts of the two acids neutralised is termed by Thomsen the *avidity* of the acid, its striving for neutralisation, but Ostwald calls it *affinity*.

In order to investigate the reaction Thomsen made use of the liberation or absorption of heat accompanying the reaction, and Ostwald made use of the changes in volume and density which accompany the change. Both chemists agree that the reaction is very rarely complete.

If one equivalent of soda ($NaOH = 39{\cdot}96$, or, in round numbers, 40 parts by weight) in dilute solution is exactly neutralised by the equivalent quantity of sulphuric or nitric acid ($\frac{1}{2}H_2SO_4 = 48{\cdot}91$, or in whole numbers 49 parts by weight and $HNO_3 = 62{\cdot}89$, or 63 in round numbers) more heat will be produced in the first than in the second case.

With sulphuric acid	15689 cals.
„ nitric acid	13617 cals.
Difference	2072

A calorie, or thermal unit, is the amount of heat required to raise the temperature of the unit weight of liquid water 1° C.

It is a general law in the mechanical theory of heat that the amount of heat evolved or absorbed in a chemical reaction depends only on the initial and final state of the system, and not on the order in which the change takes place.

The heat evolved is consequently the same when sulphuric acid and soda interact, directly forming sodium sulphate, thus:

$$(1)\ 2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O,$$

and when sodium nitrate is first formed, and afterwards converted into sulphate:

$$(2a)\ 2NaOH + 2HNO_3 = 2NaNO_3 + 2H_2O$$
$$(2b)\ 2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

It is assumed that the nitric acid in (2*b*) assumes the state in which it first occurred.

Reaction (1) yields 15689^c for each 1NaOH, but (2*a*) only yields 13617^c; therefore (2*b*) must yield the difference 2072^c for each equivalent of NaOH taking part in the reaction.

On the other hand, if the sulphate could be completely decomposed by the nitric acid, the reaction

$$Na_2SO_4 + 2HNO_3 = 2NaNO_3 + H_2SO_4$$

would yield -2072^c, *i.e.* as much heat would be absorbed as is evolved in the opposite reaction.

Thomsen found that when an equivalent of sodium nitrate ($NaNO_3$) in dilute solution is mixed with one equivalent of sulphuric acid ($\frac{1}{2}H_2SO_4$) only 288^c instead of 2072^c are evolved, and, on the other hand, one equivalent of sodium sulphate ($\frac{1}{2}Na_2SO_4$) and one equivalent of nitric acid produce -1752^c instead of -2072^c. It follows from these observations that in neither of these cases does a complete decomposition take place in accordance with the equations, but that an intermediate stage of partial decomposition ensues, which is the same in both cases.

By adding these two results together we obtain $288^c + 1752^c = 2040^c$, which agrees approximately with the difference in the heat of neutralisation of the two acids. Apparently the reactions could be represented respectively by

$$\frac{288}{2040} = 0{\cdot}14 \text{ and } \frac{1752}{2040} = 0{\cdot}86,$$

i.e. 14 per cent. of the nitrate is decomposed by the equivalent of sulphuric acid and 86 per cent. of the sulphate is decomposed by the nitric acid. But this interpretation is erroneous, for in both cases each free acid not only acts on the salt of the other acid but on its own salt with absorption of heat. By special experiments Thomsen found for the action of n equivalents of sulphuric acid on one equivalent of sodium sulphate

$$\tfrac{1}{2}(Na_2SO_4 + nH_2SO_4): -\frac{n}{n+0{\cdot}8} \cdot 1650^c,$$

and for the action of nitric acid on the nitrate

$$NaNO_3 + HNO_3 : -36^c.$$

On mixing equivalent quantities, the solution contains in a state of equilibrium

$$p\tfrac{1}{2}H_2SO_4 + (1-p)\tfrac{1}{2}Na_2SO_4 + (1-p)HNO_3 + pNaNO_3\,;$$

$$\frac{p}{1-p}\,H_2SO_4 \text{ acts on } 1Na_2SO_4\,;\ \text{therefore } n = \frac{p}{1-p},$$

and the amount of sulphate present $(1-p)\tfrac{1}{2}Na_2SO_4$ gives with the free acid a calorific effect

$$-\frac{1-p}{2}\left\{\frac{\frac{p}{1-p}}{\frac{p}{1-p}+0{\cdot}8}\right\} \cdot 1650^c = -\frac{p(1-p)}{0{\cdot}2p+0{\cdot}8} \times 1650^c.$$

In both cases the total effect is represented by

$$1.\ (1-p)\,.\,2072^c - \frac{p(1-p)}{0{\cdot}2p+0{\cdot}8}\,.\,1650^c - (1-p)36^c = 288^c.$$

$$2. -p\,.\,2072^c - \frac{p(1-p)}{0{\cdot}2p+0{\cdot}8}\,.\,1650^c - (1-p)36^c = -1752^c.$$

In these equations p is very nearly equal to $\tfrac{2}{3}$.

Replacing p by $\tfrac{2}{3}$ in equation 1, we obtain 286^c instead of 288^c and in 2, -1786^c instead of -1752^c.

The state of equilibrium is represented by the formula

$$2 \cdot \tfrac{1}{2}(H_2SO_4) + \tfrac{1}{2}(Na_2SO_4) + 1HNO_3 + 2NaNO_3\,;$$

$$\frac{p'}{p} = \chi^2\frac{q'}{q} = \frac{1}{2} = \chi^2\frac{2}{1}\,;\ \chi^2 = 0{\cdot}25\,;$$

and the avidity $Av = \chi = 0{\cdot}5$, *i.e.* when equal equivalents are taken the relative quantities of sulphuric and nitric acids neutralised are as 1 to 2.

§ 114. Avidity calculated for Molecular Weights.—These interactions are more reasonably represented by molecular formulæ, and the state of equilibrium in this case can be expressed by the formula

$$2H_2SO_4 + Na_2SO_4 + 2HNO_3 + 4NaNO_3,$$

or as sulphuric acid acts on its salts and converts the greater part of them into acid sulphates—

$$H_2SO_4 + 2NaHSO_4 + 2HNO_3 + 4NaNO_3.$$

Now let us consider what will be the result when an equal number of molecular weights (not equivalent weights) of the two acids take part in the reaction; the general formula for the state of equilibrium becomes

$$p\tfrac{1}{2}H_2SO_4 + p'\tfrac{1}{2}Na_2SO_4 + qHNO_3 + q'NaNO_3$$

and the values for the total equivalents of

$$\begin{aligned} \text{Sulphates} &= p - p' = 2 \text{ equivalents} \\ \text{Nitrates} &= q + q' = 1 \text{ equivalent} \\ \text{Salts} &= p' + q' = 1 \quad ,, \end{aligned}$$

The condition of equilibrium is

$$\frac{p'}{p} = \chi^2 \cdot \frac{q'}{q} = 0{\cdot}25\frac{q'}{q}.$$

From these four equations it follows that

$$p' = -\frac{1}{2} + \sqrt{\frac{11}{12}} = 0{\cdot}46\,;$$

$$q = p' = \ 0{\cdot}46,\ q' = 0{\cdot}54,\ p = 1{\cdot}54.$$

By introducing these values and changing the equivalent formulæ to molecular formulæ we obtain for the state of equilibrium—

$$0{\cdot}54H_2SO_4 + 0{\cdot}46NaHSO_4 + 0{\cdot}46HNO_3 + 0{\cdot}54NaNO_3.$$

The ratio between the quotients of decomposition—

$$\frac{0{\cdot}46}{0{\cdot}54} = \chi^2 \cdot \frac{0{\cdot}54}{0{\cdot}46}\,;\ \chi^2 = \left(\frac{0{\cdot}46}{0{\cdot}54}\right)^2 = 0{\cdot}73,$$

and the molecular avidity $(Av)_M = \chi = 0·85$; so that when equal molecules of nitric and sulphuric acid act on a quantity of sodium hydroxide solution equivalent to the nitric acid, 85 molecules of sodium hydrogen sulphate ($NaHSO_4$) are formed for every 100 molecules of sodium nitrate produced.

Thomsen's investigations were confirmed and further developed by Ostwald. Both investigators determined the avidity of a large number of acids. In the following table $(Av)_E$ denotes the avidity for equivalents and $(Av)_M$ the molecular avidity with the formation of acid salts. The avidity of nitric acid = 100 serves as the standard of comparison; *n* indicates the number of equivalents contained in the molecule.

—	Molecular Formula.	$(Av)_E$	*n*	$(Av)_M$
Nitric Acid	HNO_3	100	1	100
Hydrochloric Acid	HCl	98	1	98
Hydrobromic Acid	HBr	89	1	89
Hydriodic Acid	HI	79	1	79
Trichloracetic Acid	$HC_2Cl_3O_2$	80	1	80
Sulphuric Acid	H_2SO_4	49	2	83
Selenic Acid	H_2SeO_4	45	2	75
Dichloracetic Acid	$H_2C_2HCl_2O_2$	33	1	33
Oxalic Acid	$H_2C_2O_4$	26	2	40
Orthophosphoric Acid	H_3PO_4	13	3	24
Monochloracetic Acid	$HC_2H_2ClO_2$	7	1	7
Tartaric Acid	$H_2C_4H_4O_6$	5·2	2	7
Citric Acid	$H_3C_6H_5O_7$	5·0	3	9
Glycollic Acid	$HC_2H_3O_3$	5·0	1	5
Hydrofluoric Acid	HF	5·0	1	5
Formic Acid	$HCHO_2$	3·9	1	3·9
Lactic Acid	$HC_3H_5O_3$	3·3	1	3·3
Malic Acid	$H_2C_4H_4O_5$	2·8	2	4
Succinic Acid	$H_2C_4H_4O_4$	1·45	2	2·07
Acetic Acid	$HC_2H_3O_2$	1·23	1	1·23
Propionic Acid	$HC_3H_5O_2$	1·04	1	1·04
Butyric Acid	$HC_4H_7O_2$	0·98	1	0·98
Isobutyric Acid	$HC_4H_7O_2$	0·92	1	0·92

§ 115. **Relation between the Avidity and Composition of Acids.**—The numbers in the preceding table clearly show the connection between the avidity of an acid and the nature and arrangement of its atoms. The fatty acids

$$C_nH_{2n}O_2 = C_{n-1}H_{2n-1}, CO—OH$$

grow weaker as the value of *n* increases, that is, as the mass of the hydrocarbon radical united to the carboxyl increases:

		Av
Formic Acid	$H-CO-OH$	3·9
Acetic „	$CH_3-CO-OH$	1·23
Propionic „	$C_2H_5-CO-OH$	1·04
Butyric „	$C_3H_7-CO-OH$	0·98

The avidity is increased by replacing hydrogen by hydroxyl (OH).

		Av
Acetic Acid . . .	$CH_3-CO-OH$	1·23
Glycollic „ . . .	$HO-CH_2-CO-OH$	5
Propionic „ . . .	$C_2H_5-CO-OH$	1·04
Lactic „ . . .	$HO-C_2H_4-CO-OH$	3·3

		$(Av)_E$	$(Av)_M$
Succinic Acid .	$HO-CO-C_2H-{}_4CO-OH$	1·45	2·07
Malic „ .	$HO-CO-C_2H_3(OH)-CO-OH$	2·8	4·0
Tartaric „ .	$HO-CO-C_2H_2(OH)_2CO-OH$	5·2	7·3

It is greatly increased when H_2 is replaced by O.

		(Av)	$(Av)_M$
Glycollic Acid. . .	$HO-CH_2-CO-OH$	5	5
Oxalic „ . . .	$HO-CO-CO-OH$	26	40

The same effect is produced by replacing hydrogen by chlorine.

		Av
Acetic Acid	$CH_3-CO-OH$	1·23
Monochloracetic Acid. . .	$CH_2Cl-CO-OH$	7
Dichloracetic „ . . .	$CHCl_2-CO-OH$	33
Trichloracetic „ . . .	$CCl_3-CO-OH$	80

All these examples show that the facility with which a chemical change takes place is determined, not only by the nature and arrangement of the atoms directly taking part in the reaction, but is also influenced by other more distant atoms in the chain, and frequently their influence is so powerful as to preponderate over that of all the others.

§ 116. **Connection between Avidity and other Properties of the Acids.**—The property termed *avidity* or relative affinity determines the behaviour of the acid in almost all its actions.

The inversion of sugar by acids in dilute aqueous solution mentioned in § 108, where the acid remains unchanged, the analogous decomposition of ethereal salts soluble in water by dilute acids, and many similar reactions, take place with a velocity which is directly proportional to the avidity. A relation also exists between the avidity, the rate of diffusion, and the closely allied electric conductivity of acids. The strength of an acid is almost directly proportional to its rate of diffusion and to its conductivity.

This surprising connection between chemical and physical properties is explained by the fact that the apparently stronger acids are those which dissociate most easily, and in proportion to the facility with which the acid dissociates into ions not only is its power of taking part in chemical changes raised, but its conductivity and other properties are in like manner increased.

What we term affinity or avidity is nothing more than the facility of entering into reactions, the mobility. We can therefore do without the notion of strong or weak chemical affinity in these speculations, although at the present time we cannot safely substitute another cause for the combination of the atoms. Our present views are essentially different from the earlier views. What was formerly ascribed to a stronger attractive force is now accounted for as a result of greater mobility.

§ 117. **Influence of Insolubility and Volatility on Chemical Change.**—C. L. Berthollet has pointed out that an act of double decomposition is materially influenced by the state of aggregation of the bodies taking part in the reaction. Berthollet maintained that when a compound separates out in an insoluble or volatile form it then loses all influence on the reaction. He explained, for example, the nearly perfect precipitation of sulphuric acid by barium salts and similar changes by assuming that the two acids—for instance, sulphuric and hydrochloric acids—distribute themselves between the base, according to the relative quantities in which they are present and in the ratio of their affinities. But the state of equilibrium produced is disturbed by the precipitation of insoluble barium sulphate, and consequently a new distribution of the acids takes place, and this process continues until there is either no barium salt or no sulphuric acid in the solution.

In this particular instance, owing to the resistance which barium sulphate offers to chemical change, this hypothesis corresponds fairly well with what actually takes place; but, as a general rule, this is not the case, as the insoluble precipitates do not cease to interact with the compounds still remaining in solution.

The simplest problem which offers itself for our consideration is when two of the four bodies interacting on each other are soluble and two insoluble. In this case Guldberg and Waage's theory can be applied with a slight modification. Of the four bodies A . B . A′ . B′ (see § 111) taking part in the reactions let A′ and B′ be insoluble. The state of equilibrium is represented by $pA + p'A' + qB + q'B'$; the equation for the quotients of decomposition, $\frac{p'}{p} = \chi^2 \frac{q'}{q}$, is simplified by the fact that an increase in the quantities p' and q' of the insoluble compounds does not exert any perceptible influence. These quantities may therefore be regarded as invariable, provided that not too small a quantity of each of these bodies is present. Let $\chi^2 \frac{q'}{p'} = \gamma =$ constant; then $q = \gamma . p$; that is to say, in the state of equilibrium a definite relation exists between the quantities of the two soluble substances in the solution. This condition is established when the quantity of A acting on the insoluble B′ is equal to the amount of B interacting with A′ in the same interval of time. In order that this state of equilibrium may be rapidly attained the liquid must be brought into intimate contact with the precipitate by boiling or by shaking. The coefficient γ depends not only on the nature of the interacting compounds but also on the concentration and temperature, and is often greatly influenced by these conditions. The more or less crystalline character of the precipitate frequently exerts a considerable influence.

Guldberg and Waage allowed mixtures of barium sulphate and potassium carbonate, and barium carbonate and potassium sulphate, to interact for a year at 3° C. The substances were originally present in the proportions—

(*a*) $1BaSO_4 + 1K_2CO_3 + 100H_2O$
(*b*) $1BaCO_3 + 1K_2SO_4 + 100H_2O$.

After a year the solutions contained—

(*a*) $0{\cdot}959K_2CO_3 + 0{\cdot}041K_2SO_4$; $\gamma = 23{\cdot}4$
(*b*) $0{\cdot}929K_2CO_3 + 0{\cdot}071K_2SO_4$; $\gamma = 13{\cdot}1$

and consisted, therefore, almost entirely of carbonate: in (*a*) $23{\cdot}4K_2CO_3$ and in (*b*) $13{\cdot}1K_2CO_3$ to each molecule of K_2SO_4. The state of equilibrium had not been reached in this long period, as is evident from the marked difference in the values of γ.

At 100° the interaction goes on more rapidly, but γ is much smaller, *i.e.* there is much more sulphate in solution.

In three days $1BaSO_4 + 1K_2CO_3 + 100H_2O$
yielded $0{\cdot}76K_2CO_3 + 0{\cdot}24K_2SO_4$; $\gamma = 3{\cdot}2$;
and $1BaCO_3 + 1K_2SO_4 + 100H_2O$
in the same time produced $0{\cdot}72K_2CO_3 + 0{\cdot}28K_2SO_4$; $\gamma = 2{\cdot}6$.
Here the state of equilibrium has been nearly attained.

A strong solution contains more sulphate, a dilute solution more carbonate. This agrees with the directions H. Rose gave many years ago for decomposing barium sulphate by boiling with a strong solution of potassium carbonate, and renewing the potassium carbonate solution when it contained a certain quantity of sulphate.

The chromates behave like the sulphates. According to James Morris, potassium carbonate and barium chromate interact until the solution contains $10K_2CO_3$ if cold, or $3{\cdot}75K_2CO_3$ if boiling, for each K_2CrO_4. Here, again, as the temperature rises γ decreases, and with it the amount of carbonate in solution.

According to Watson Smith, the insoluble calcium oxalate is very slightly attacked by sodium carbonate, but calcium carbonate is almost completely decomposed by sodium oxalate. The behaviour of the corresponding compounds of strontium, barium, and lead is exactly the reverse of that exhibited by calcium carbonate and oxalate.

§ 118. **One Insoluble Substance.**—The problem is not quite so simple when only one of the interacting compounds is insoluble. When aqueous solutions of oxalic acid and calcium chloride are mixed together, calcium oxalate is precipitated, and free hydrochloric acid, oxalic acid, and some calcium chloride remain in solution. The state of equilibrium is represented by the formula—

$$pH_2Cl_2 + p'CaCl_2 + qH_2C_2O_4 + [q'CaC_2O_4].$$

For the sake of uniformity the formula for hydrochloric acid is doubled. The formula of the insoluble compound is placed in brackets. Two reactions maintain equilibrium, viz.:

$$CaCl_2 + H_2C_2O_4 = H_2Cl_2 + [CaC_2O_4]$$

and

$$H_2Cl_2 + [CaC_2O_4] = CaCl_2 + H_2C_2O_4.$$

The frequency with which the first reaction takes place increases with the number of particles of the interacting bodies in solution; it is therefore proportional to the product $p' \times q$. The value of q', which is always relatively large, has no perceptible influence on the frequency of the reaction, and the relation between the reaction and the number p of acid equivalents is far from simple. It is certain that calcium chloride and oxalic acid can only exist together in solution in very small quantities, so the first reaction preponderates over the second. When an excess of oxalic acid or of calcium chloride is used (according to Ostwald both act in the same way), the first reaction takes place to the almost entire exclusion of the second.

§ 119. **Action of Mass in Gases.**—If one of the products of decomposition in a solution is a gas, and entirely escapes, it ceases to exert any further influence. But if the whole or a part of it remains absorbed, then the absorbed gas behaves like any other substance in solution—that is to say, it can reverse the reaction which led to its formation.

Gases are frequently formed by the dissociation of compounds in solution, *e.g.* carbonic anhydride is evolved from bicarbonates. If all the gas escapes the decomposition is complete and all the bicarbonate changes into carbonate. Such a change is more likely to occur in a hot than in a cold solution. If carbonic anhydride remains in solution, then some bicarbonate will remain undecomposed or will be reformed. According to Hüfner's observations, the red colouring matter of the blood, so necessary to the life of man and the higher animals, loses the oxygen with which it is combined in a similar way unless there is at least a small quantity of free oxygen dissolved in the blood. If the free oxygen is removed, fresh oxygen will be formed by dissociation of the colouring matter. This process may be repeated until the red colouring matter is completely decomposed, so that by means of the air-pump all the oxygen can be removed, although the greater part of it is in a state of chemical combination, and only a small fraction of it is physically absorbed.

Guldberg and Waage's law or a similar law is probably valid when all the bodies taking part in the reaction are gaseous. But experimental proof of this problem has only been adduced in a few special cases. The first experiments in this direction (or, indeed, on the action of mass since the time of Berthollet) were made by Bunsen, who proved that when two combustible gases are mixed with a quantity of oxygen insufficient for their complete combustion the amount of oxygen combining with either gas is proportional to the amount of that gas present. In the case of a mixture of carbon monoxide and hydrogen the oxygen will be equally divided between the two gases if the mixture consists of six volumes of carbon monoxide to one of hydrogen. In a mixture of equal volumes of the two gases the hydrogen takes up three or four times as much oxygen as the carbon monoxide. The quantities change in the manner indicated by Guldberg and Waage's law, but they do not obey this law as closely as might be supposed. Recent investigations of Harold Dixon have shown that the process is much less simple than was formerly thought to be the case. Perfectly dry carbon monoxide burns in oxygen with great difficulty, although it burns readily when it is mixed with aqueous vapour; the aqueous vapour is reduced and the resulting hydrogen is again oxidised—[1]

$$CO + H_2O = CO_2 + H_2;$$
$$2H_2 + O_2 = 2H_2O.$$

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[1] *Vide* para. 92.

Probably the law of Guldberg and Waage is valid for the first process, providing that the temperature is sufficiently high to prevent the water depositing.

The state of equilibrium is $pCO + p'CO_2 + qH_2 + q'H_2O$ and

$$\frac{p'}{p} = \chi^2 \cdot \frac{q'}{q}.$$

As the second reaction can only be reversed at a very high temperature the law does not apply to this case. Mass exerts considerable influence in the interaction of gases and solids, *e.g.* the oxidation of red-hot charcoal by steam, when the chief products are carbonic anhydride, hydrogen, and a small quantity of carbon monoxide, but a portion of the steam remains undecomposed.

§ 120. **Exceptions to Guldberg and Waage's Law.**—Unexpected deviations from Guldberg and Waage's law are occasionally met with. For example, A. Bonz found that the formation of an amide by the action of ammonia on an ethereal salt is a reversible reaction.

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Ethyl acetate}}{C_2H_5OCOCH_3} = \underset{\text{Acetamide}}{NH_2COCH_3} + \underset{\text{Alcohol}}{HOC_2H_5}$$

At temperatures above 100° alcohol and acetamide interact, yielding ethyl acetate and ammonia. The proportion of ethereal salt produced increases with the temperature and with the molecular weights of the alcohol and amide.

The influence of mass is in accordance with the law of Guldberg and Waage. The value of χ^2, however, is only constant when equal molecules of ethereal salt and ammonia are present, *i.e.* in the proportion in which they are formed by the action of alcohol on the amide. The addition of an excess of ammonia retards the decomposition of the amide by alcohol to a greater extent than it should do in accordance with Guldberg and Waage's law, whereas the retarding by the ether is less than is required by the law. The two reacting bodies do not in this instance act in a similar manner, as is usually the case. Such cases in all probability occur more frequently than have hitherto been observed.

§ 121. **Non-reversible Reactions.**—The law of Guldberg and

Waage does not apply to non-reversible reactions. In these cases the rule appears to be that the quantity of every reacting substance exerts an influence, but the influence produced by the mass varies with different substances. Menschutkin has shown that the formation of acetanilide from aniline and acetic acid—

$$\underset{\text{Aniline}}{NH_2.C_6H_5} + \underset{\text{Acetic acid}}{HOCOCH_3} = \underset{\text{Acetanilide}}{NHC_6H_5.CO.CH_3} + \underset{\text{Water}}{HOH}$$

is greatly facilitated by an excess of acetic acid, whereas an excess of aniline delays the operation, but increases the amount of the product. If Guldberg and Waage's law were valid both bodies would act in the same way. That it does not apply in this instance is probably due to the fact that the acetic acid dissociates, and that the aniline either does not dissociate or dissociates only to a slight extent.

A still more striking example of the difference in the influence of two interacting bodies on a reaction is afforded in the nitration of aromatic organic compounds, *e.g.*—

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Nitric acid}}{HONO_2} = \underset{\text{Nitro-benzene}}{C_6H_5.NO_2} + \underset{\text{Water}}{H_2O}$$

The reaction is facilitated by increasing the amount of nitric acid, but it is delayed by the addition of benzene and also by the products of the decomposition—namely, water and nitro-benzene. An increased quantity of acid not only increases the absolute, but also the relative quantity, *i.e.* the percentage of acid taking part in the interaction. According to A. Kessler, by taking double the theoretical quantity of nitric acid, the yield of nitro-benzene in the first quarter of an hour is increased fourfold; and if the amount of nitric acid is trebled, the yield will be ninefold. The quantity of nitro-benzene increases in proportion to the square of the quantity of acid used. In order to make this observation it is necessary to mix the benzene with its equivalent of nitro-benzene and to keep the mixture cold in order to moderate the reaction, which would otherwise take place with explosive violence.

Without doubt the complete difference in the influence of these two interacting compounds is due to the fact that the power of dissociation is possessed by nitric acid in a very high degree, and not at all by benzene. Nitric acid dissociates according to the equation

$$2HO.NO_2 = N_2O_5 + H_2O$$

and does not form the electrolytic ions H and NO_3.

The anhydride then attacks the benzene thus:

$$NO_2.O.NO_2 + 2C_6H_6 = 2C_6H_5.NO_2 + H_2O.$$

Diluting the acid with water, nitro-benzene, or even with benzene, tends to prevent the decomposition of the acid into anhydride and water, and the weak acid steadily grows weaker, and finally ceases to nitrate. The ease with which the nitration is effected also depends on the nature and composition of the organic body. When a portion of the hydrogen in benzene is replaced by other elements or radicals, the operation of nitration may be facilitated, or it may be rendered more difficult, and even impossible. This depends on the nature and the position of the elements replacing the hydrogen.

§ 122. **Contact Action.**—It occasionally happens that two or more bodies can only interact in the presence of a third, and this third substance either remains unchanged or experiences a change itself. Phenomena of the first class are termed *catalysis* by Berzelius and *contact action* by Mitscherlich. The characteristic feature of this class of phenomena is that a small quantity of the substance which remains unchanged can bring about the decomposition of a very large quantity, frequently of an unlimited quantity, of another compound.

The ignition of hydrogen and oxygen by finely divided platinum is a simple example of this contact action. The action of the metal depends on the property which platinum possesses of condensing gases on its surface and of bringing them into such intimate contact that combination ensues. Contact action is a term which is well adapted to describe this class of phenomena. It is, of course, open to question whether the metal does act only by contact, or whether it forms an unstable compound either with oxygen or, like palladium, with hydrogen.

In other cases the participation of the 'contact substance' in the interaction has been definitely proved. Take, for example, the 'carriers of oxygen.' As the oxidation of sulphurous acid by the oxygen of the air takes place very slowly, nitric oxide is used as a carrier of oxygen in the leaden chamber of the vitriol works. The nitric oxide, NO, is oxidised at the expense of the oxygen of the atmosphere to the peroxide, NO_2, which oxidises the sulphurous acid and is reconverted into nitric oxide. The reaction is not quite as simple as it is here depicted. In the first place, nitro-sulphonic acid (the crystals of the leaden chamber) $HO—SO_2—NO_2$ is first formed from nitric oxide, oxygen, steam, and sulphur dioxide. This compound decomposes, yielding sulphuric acid and oxides of nitrogen—

$$2HO—SO_2—NO_2 + H_2O = 2HO—SO_2—OH + NO_2 + NO.$$

The sulphates and other salts of manganese, copper, iron, and other metals act as carriers of oxygen to aqueous solutions of sulphurous acid, as they are reduced by the sulphurous acid and reoxidised by the atmospheric air. A cold solution of oxalic acid is not oxidised by chromic acid, except in the presence of a manganese salt, which reduces the chromic acid and oxidises the oxalic acid. Manganese sulphate also acts as a carrier of oxygen when oxalic acid is oxidised by permanganic acid. Indigo effects the oxidation of an alkaline solution of grape sugar by acting as a carrier of atmospheric oxygen, for the indigo is reduced to indigo-white by the grape sugar, but at once unites with oxygen and forms indigo-blue again.

The formation of ethyl ether from alcohol and sulphuric acid was formerly considered to be an example of catalytic or contact action—

$$2C_2H_5.OH = (C_2H_5)_2O + H_2O.$$

But Williamson proved that the sulphuric acid takes part in the change, thus :

$$\underset{\text{Alcohol}}{C_2H_5.OH} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Ethyl sulphuric acid}}{C_2H_5HSO_4} + \underset{\text{Water}}{H_2O}$$

$$C_2H_5.OH + C_2H_5.HSO_4 = \underset{\text{Ether}}{C_2H_5.O.C_2H_5} + H_2SO_4.$$

The sulphuric acid does not act merely by its presence, but takes part in the interaction and is formed again. It is probable that something similar takes place in the case of the apparently simple decompositions mentioned in § 108. The decomposition of cane sugar into dextrose and lævulose is probably preceded by the formation of corresponding ethereal salts with the inverting acid, which are in their turn decomposed by water.

Emmerling observed and explained a very remarkable case of apparent contact action. Oxalic acid scarcely attacks crystalline calcium carbonate, *e.g.* marble. A thin insoluble crust of calcium oxalate forms on the surface of the marble, which prevents any further action taking place, but on the addition of a very small quantity of nitric acid or a nitrate the marble is rapidly attacked and converted into calcium oxalate. Apparently it is the nitric acid or the nitrate which incites the oxalic acid to attack the calcium carbonate, but in reality it is the nitric acid which was added or was liberated from the nitrate by the oxalic acid that attacks the marble, forming calcium nitrate. The oxalic acid interacts, forming calcium oxalate and liberating nitric acid.

Interactions which apparently take place between two substances but require the presence of a third body, are of frequent occurrence. Many metals remain unaltered in dry air which rust or oxidise in a damp atmosphere. M. Traube has shown that water takes part in this process of oxidation; a metallic hydroxide and hydrogen peroxide are first formed according to the equation—

$$Zn + 2HO \;\vdots\; H + O_2 = ZnO_2H_2 + H_2O_2.$$

The metal decomposes the water, forming hydroxyl (HO—) and hydrogen, but the latter unites with a molecule of oxygen. The molecule of oxygen consists of two atoms, and at the low temperature the hydrogen is unable to effect their separation.

The hydroxide loses water and passes into oxide, the hydrogen peroxide loses oxygen, forming water. In this way the water which took part in the interaction re-appears as water when the reaction is completed.

Certain bodies act as carriers of chlorine in a similar way to the oxygen carriers. Pure nitro-benzene is practically unattacked by chlorine, but in the presence of anhydrous ferric chloride substitution of the hydrogen by chlorine takes place; but the ferric chloride remains unchanged in quantity and has apparently taken no part in the reaction.

When bromine is substituted for chlorine the following reaction takes place, according to A. Scheufelen :

$$Br_2 + C_6H_5NO_2 + FeCl_3 = Br.C_6H_4.NO_2 + HCl + FeCl_2Br$$

and the analogous change in the case of chlorine is

$$Cl_2 + C_6H_5NO_2 + FeCl_3 = Cl.C_6H_4.NO_2 + HCl + FeCl_2.Cl.$$

The chlorine of the ferric chloride unites with an atom of hydrogen of the benzene to form hydrochloric acid, and both atoms are replaced by free chlorine or bromine. All three bodies consequently take part in the interaction.

The conversion of diazo-amido compounds into amido-azo bodies by the presence of the salt of an amine is apparently another example of contact action, in which the small amount of amine salt taking part in the reaction appears at the end of the action in unaltered amount ; *e.g.*

$$\underset{\text{Diazo}}{C_6H_5N_2} \vdots \underset{\text{amidobenzene}}{HNC_6H_5 + H} \vdots \underset{\text{Aniline}}{C_6H_4NH_2} = \underset{\text{Amidoazobenzene}}{C_6H_5N_2C_6H_4NH_2} + \underset{\text{Aniline}}{H_2NC_6H_5}$$

The aniline which appears at the end of the reaction is not that which was employed to produce the change, but that which has been split off from the diazo-compound decomposed.

The numerous and varied forms of fermentation were formerly regarded as cases of catalytic action. It was believed that simple contact with the ferment, *e.g.* yeast, brought about the decomposition of the fermentable substance, sugar. Fermentation is now considered to be due to the action of minute living organisms, which devour the fermentable substance for their nourishment and excrete the decomposition products. The yeast ferment feeds on sugar and produces carbon dioxide and alcohol. The process is much more complicated than was formerly supposed to be the case.[1]

This example, taken from a large class of similar phenomena, clearly shows that those changes which were formerly described as the result of contact action must be generally regarded as the interaction of three or more different bodies, or are even much more complex reactions. Berzelius explained this class of phenomena by the hypothesis of a special catalytic force contained in those substances which apparently take no part in the interaction. This hypothesis is now known to be unnecessary and superfluous.

§ 123. **Kinetic Nature of Affinity.**—An examination of the various forms of chemical change as described in the preceding paragraphs leads of necessity to the conclusion that the hypothesis of an attractive force known as affinity, such as was formerly accepted and even survives to the present time, is of little or no use in explaining chemical phenomena.

We might conclude from the fact that cupric sulphate is reduced to a cuprous salt by sulphurous acid that sulphurous acid has a stronger affinity for oxygen than copper has in the form of cuprous oxide; we should consequently expect that cuprous oxide will take up oxygen from the air less readily than sulphurous acid does. As observation shows that the reverse is the case, we come to the conclusion that this view of the matter is incorrect; nor is the explanation satisfactory in many other cases. We have gradually receded from the idea of a static state of equilibrium of the atoms brought about by their powers of affinity, and we now consider the atoms, and the molecules which are built up of atoms, as particles in an active state of movement. Their relations to each other are essentially determined by the magnitude and form of their movements. Chemical theories grow more and more kinetic, and although, partly from habit and partly from want of a better expedient, the existence of an attractive force between the atoms is frequently assumed in explaining chemical phenomena, still this assumption is only employed in the conviction that the hypothetical affinity is merely an expression for the real though imperfectly known cause of the internal cohesion of chemical compounds.

---

[1] Buchner has recently succeeded in showing that a liquid can be obtained from yeast by pressure which contains an enzyme-like body capable of producing alcoholic fermentation (*Ber. der deut. chem. Ges.* 30, 117, 1110, 2668).

APPENDIX

MOLECULAR COMPLEXITY OF LIQUIDS

At approximately equal intervals of temperature below their critical temperature, all normal liquids possess equal molecular surface energy. Molecular surface energy is the product of the surface tension and molecular surface, *i.e.* the surface on which equal numbers of molecules are supposed to be uniformly distributed, $= \frac{2}{3}$ power of molecular volume of liquid.

For unassociating liquids $\gamma(\mathrm{M}v)^{\frac{2}{3}} = \kappa(\tau - d)$, when τ is the temperature measured downward from the critical temperature and d is a constant (approximately 5°) to be deducted from τ, $\kappa = 2{\cdot}121$ for non-associating liquids.

In the case of associating liquids the degree of complexity, x, is calculated by Ramsay[1] by means of the equation

$$\frac{2{\cdot}121}{\kappa}(1 + \mu\tau)^{\frac{3}{2}} = x$$

and by Van der Waals[2] by the equation

$$x^{\frac{3}{2}} = \frac{\kappa(\tau' - \tau) + \gamma(mv)^{\frac{2}{3}}}{\gamma(mv)^{\frac{2}{3}}}$$

Ramsay finds the following values for x at 20°:

Methyl alcohol,	2·32	Water,	1·64
Ethyl alcohol,	1·65	Acetic acid,	2·13

J. Traube[3] deduces the molecular complexity of liquids or of solids in solution from their molecular volumes.

---

[1] *Chem. Soc. Trans.* 1893, 1092; *Roy. Soc. Proc.* 1894, lvi. 162.

[2] *Zeit. für phys. Chem.* xiii. 657.

[3] *Ber. d. deut. chem. Ges.* xxviii. 2722, 2924, 3297; xxix. 1023, 2732; xxx. 265.

The molecular volume of a compound exceeds the sum of the atomic volumes of its constituents by 25·9 c.c. at 15°, $\frac{m}{d} - \Sigma = 25{\cdot}9$. Traube calls this constant the co-volume. The following are the most important atomic volumes:

C	9·9	S'	15·5	CN	13·2	Na . .	3·1
H	3·1	S''	15·5	N'''	1·5	C_6 nucleus	− 8·1
O'	2·3	S°	10–11·5	N^v	10·7 circa	C_4S „	−11·4
O''	5·5	F	5·5	N°	8·5–10·7	1= .	− 1·7
O^v	5·5	Cl	13·2	P'''	17 circa	1≡ .	− 3·4
O^b	0·4	Br	17·7	P^v	28·5 „		
		I	21·4				

O' and S' indicate oxygen and sulphur in the groups OH, SH.

O'' and S'' doubly linked to carbon, as in the aldehydes and ketones.

O^v oxygen uniting two C atoms together, ether.

O^b one oxygen atom in a carboxyl group.

S° N°, S and N in sulpho- or nitro-groups. 1= = double linking, 1≡ = treble linking.

The association factor x is calculated from the co-volume c. If at 15° $c = 25{\cdot}9$, then $x = 1$; but if $c = 12{\cdot}95$, then $x = 2$. The following values for x show that the results obtained by Traube's method are not identical with Ramsay's:

Water,	3·06	Formic acid,	1·8	Ethyl alcohol,	1·67
Glycol,	1·88	Acetic acid,	1·56	Benzene,	1·18
Glycerol,	1·82	Methyl alcohol,	1·79	Toluene,	1·08

ARGON AND HELIUM.

Lord Rayleigh's observation that the nitrogen prepared by the decomposition of nitrogenous compounds differed in density from the 'nitrogen' extracted from atmospheric air led to the discovery of the existence of the element Argon.[1] In the following year Ramsay[2] discovered another gaseous element in the mineral cleveite. The spectroscope revealed the identity of this element with the body Helium, discovered in 1868 by Lockyer in the solar chromosphere.

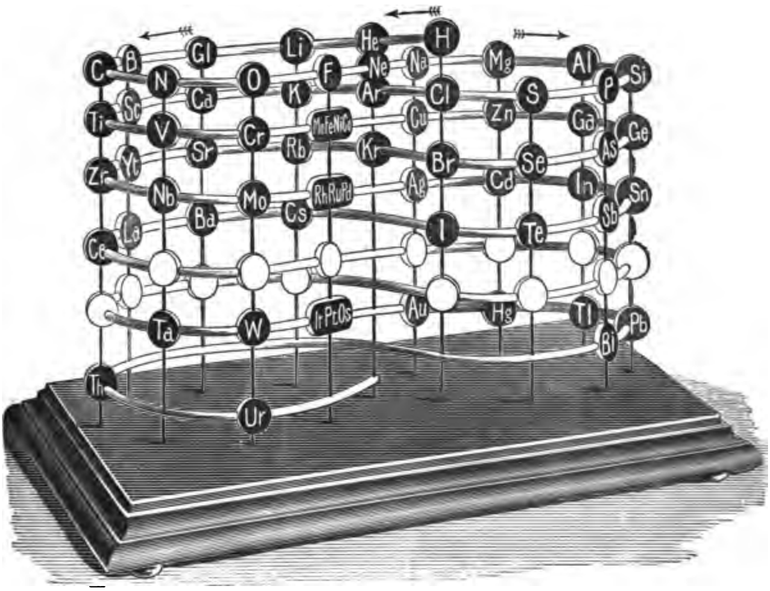
Argon and helium are remarkable for their chemical inertness. They do not combine with any other chemical elements. The molecules of these gases are monatomic, like mercury. The densities are approximately 2 and 20 respectively, consequently the atomic weights are 4 and 40. During the present year two new constituents of the atmosphere have been discovered by Professor Ramsay,[1] viz. Neon and Krypton. They resemble argon inasmuch as their molecules are monatomic. The atomic weights of these elements have not been determined. They are probably about 22 and 80.

---

[1] Ramsay and Rayleigh, *Phil. Trans.* 1895, 187.

[2] *Chem. Soc. Trans.* 1895, 684.

If the atomic weight of argon is greater than 39—apparently it is nearly 40—argon will occupy a position in the Periodic System



between potassium and calcium. That is to say, this inactive gas would occupy a position between two solid elements exhibiting the characteristic properties of the metals. It would also displace calcium and each of the following elements in the series. The elements would cease to form groups of similar valency.

The existence of helium, argon, and probably of krypton and neon, demands a modification of Mendeléeff's or Lothar Meyer's arrangement of the elements. Crookes[2] proposes that instead of arranging the elements in the form of a spiral, they should be arranged in a figure of eight, as shown in the above illustration.

---

[1] *Proc. Roy. Soc.* 1898, 405.

[2] *Ibid.* 1898, 408.

Each loop is divided into eight equal parts. The vertical height is divided into 240 equal parts on which the atomic weights are plotted. The elements occurring in the same column form natural groups.

H	He	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S
Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn Fe Ni Co	Cu	Zn	Ga	Ge	As	Se
Br	Kr	Rb	Sr	Yt	Zr	Nb	Mo	Rh Ru Pd	Ag	Cd	In	Sn	Sb	Te
I		Cs	Ba	La	Ce	—	—	—	—					
					—	Ta	W	Ir Pt Os	Au	Hg	Tl	Pb	Bi	
					Th	—	Ur							

In this arrangement He, Ar, Kr are found on the neutral line —*i.e.* at the points where the coils of the figure 8 intersect.

THE ATOMIC WEIGHTS OF THE ELEMENTS

Great importance is undoubtedly attached to an exact knowledge of the ratio between the atomic weights of the elements hydrogen and oxygen, and during the past decade many chemists have in various ways attempted to obtain this knowledge with the utmost degree of accuracy. Amongst these may be mentioned Kaiser,[1] Noyes,[2] Cooke and Richards,[3] and E. W. Morley,[4] whose methods depend upon the gravimetric synthesis of water, whilst Scott[5] has determined the proportion by volume in which hydrogen and oxygen combine, employing large volumes of these gases, each being prepared by a variety of methods. Scott concludes the proportion by volume to be 2·00245 : 1, and, combining this with the density of oxygen as ascertained by Lord Rayleigh,[6] the atomic weight of oxygen is 15·862 when hydrogen is unity, or hydrogen is 1·0078 when oxygen is 16. Morley's results give the ratio of H : O as 1 : 15·879±0·0011 or 1·00762 : 16. Thomsen[7] has also sought to arrive at this ratio from the synthesis of ammonium chloride, and concludes that the ratio of H : O is 1 : 15·869±0·0022 or 1·008255 : 16. It would appear, therefore, that the atomic weight of oxygen lies between the values 15·87–15·88. The question as to whether atomic weights should be expressed in terms of that of hydrogen ($H = 1$) or that of oxygen ($O = 16$) has been decided by a committee—consisting of Landolt, Seubert, and Ostwald, of the 'deutschen chemischen Gesellschaft'—in favour of the latter.

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[1] *Amer. Chem. Jour.* (1891), xiii. 253.

[2] *Ibid.* (1891), xiii. 354.

[3] *Ibid.* (1887), x. 81–110, 191–196.

[4] *Amer. Chem. Soc.* xvii. 267–275.

[5] *Proc. Roy. Soc.* liii. 130–134.

[6] *Ibid.* 134–149.

[7] *Berichte*, 1894, pp. 2770–2773.

ATOMIC WEIGHTS, RECALCULATED BY F. W. CLARKE

NOTE.—Where the value for the atomic weight of an element is the mean of the results of several observers, the authorities are not given.

—	H = 1	O = 16	—
Aluminium	26·91	27·11	J. W. Mallet[1]
Antimony	119·52	120·43	Cooke[2]
Argon	—	39·84	Rayleigh and Ramsay[3]
Arsenic	74·44	75·01	Dumas, Pelouze
Barium	136·39	137·43	Richards[4]
Beryllium	9·01	9·08	Krüss, Nilson, Pettersson
Bismuth	206·54	208·11	Schneider[5]
Boron	10·86	10·95	—
Bromine	79·34	79·95	Stas
Cadmium	111·10	111·95	—
Caesium	131·89	132·89	Bunsen, Johnson, Allen, Goddefroy
Calcium	39·76	40·07	—
Carbon	11·91	12·00	Scott[6]
Cerium	138·3	139·35	Wyrouboff and Verneüil[7]
Chlorine	35·18	35·45	Stas
Chromium	51·74	52·14	—
Cobalt	58·55	58·99	Richards and Baxter[8]
Copper	63·12	63·60	Richards[9]
Erbium	165·06	166·32	Cleve[10]
Fluorine	18·91	19·06	—
Gadolinum	155·57	156·76	Bettendorff
Gallium	69·38	69·91	Boisbaudran[11]
Germanium	71·93	72·48	Winkler[12]
Gold	195·74	197·23	—
Helium	—	4·	Rayleigh, Ramsay[13]
Hydrogen	1·00	1·008	—
Indium	112·99	113·85	Winkler[14]
Iodine	125·89	126·85	Stas
Iridium	191·66	193·12	Seubert,[15] Joly[16]
Iron	55·6	56·02	Berzelius, Erdmann, Maumené
Lanthanum	137·59	138·64	—
Lead	205·36	206·92	Stas
Lithium	6·97	7·03	Stas

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[1] *Phil. Trans.* 1880, p. 1003.

[2] *Proc. Amer. Acad.* v. 13; *Berichte*, xiii. 951.

[3] *Phil. Trans.* clxxxvi. 220, 238.

[4] *Proc. Amer. Acad.* xxix. 55.

[5] *Jour. für prak. Chem.* [2] l. 461.

[6] *Chem. Soc.* 1897, p. 550.

[7] *Bull. Soc. Chim.* [3] xvii. 679; *Compt. rend.* cxxv. 950 and 1180.

[8] *Proc. Amer. Acad.* xxxiii. 115.

[9] *Ibid.* xxii. 346; xxiii. 177; xxv. 195; xxvi. 240, 276.

[10] K. Svensk, *Vet. Akad. Hardlingar*, No. 7, 1880.

[11] *Ann. chem. Pharm.* cclxx. 376. *Chem. Soc.* 1878, p. 646.

[12] *Jour. für prak. Chem.* [2] xxxiv. 177.

[13] *Chem. Soc. Trans.* 1895, p. 700.

[14] *Ibid.* cii. 282.

[15] *Berichte*, 1878, p. 1767.

[16] *Compt. rend.* cx. 1131.

ATOMIC WEIGHTS RECALCULATED—*continued*

—	H=1	O=16	—
Magnesium . .	24·19	24·38	Marignac,[1] Richards and Parker[2]
Manganese . .	54·57	54·99	Marignac,[3] Dewar & Scott,[4] Weeren
Mercury . .	198·49	200	Hardin[5]
Molybdenum .	95·26	95·99	Seubert and Pollard[6]
Neodidymium .	139·70	140·80	Welsbach[7]
Neon . . .	—	—	—
Nickel . . .	58·24	58·69	Richards[8]
Niobium . .	93·02	93·73	Marignac[9]
Nitrogen . .	13·93	14·04	Stas
Osmium . .	189·55	190·99	Seubert[10]
Oxygen . .	15·88	16	Rayleigh,[11] Morley[12]
Palladium . .	105·56	106·36	Schrötter,[13] Van der Plaats[14]
Phosphorus . .	30·79	31·02	—
Platinum . .	193·41	194·89	Seubert,[15] Halberstadt[16]
Potassium . .	38·82	39·11	Stas
Praseodidymium .	142·5	143·6	Welsbach[17]
Rhodium . .	102·23	103·01	Seubert and Kobbe[18]
Rubidium . .	84·78	85·43	—
Ruthenium . .	100·91	101·68	Joly[19]
Samarium . .	149·13	150·26	—
Scandium . .	43·78	44·12	Cleve,[20] Nilson[21]
Selenium . .	78·42	79·02	—
Silicon . . .	28·18	28·40	Thorpe[22]
Silver . . .	107·11	107·92	Stas
Sodium . .	22·88	23·05	Stas
Strontium . .	86·99	87·65	Richards[23]
Sulphur . .	31·83	32·07	Stas
Tantalum . .	181·45	182·84	Marignac[24]
Tellurium . .	126·52	127·49	[25]

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[1] *Arch. Sci. Phys. et Nat.* [3], x. 206.

[2] *Zeitsch. anorg. Chem.* xiii. 81.

[3] *Arch. Sci. Phys. et Nat.* [3], x. 21.

[4] *Proc. Roy. Soc.* xxxv. 44.

[5] *Amer. Chem. Soc.* xviii. 1003.

[6] *Zeit. anorg. Chem.* viii. 434.

[7] *Monatsh. Chem.* vi. 490.

[8] *Proc. Amer. Acad.* xxxiii. 97.

[9] *Arch. Sci. Phys. et Nat.* [2], xxiii. 1865.

[10] *Berichte,* xxi. 1839; *Ann. d. Chem.* cclxi. 258.

[11] *Proc. Roy. Soc.* l. 448.

[12] 'On the Density of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights.' *Smithsonian Contributions to Knowledge,* 1895.

[13] *J. prakt. Chem.* liii. 435.

[14] *Compt. rend.* c. 52.

[15] *Berichte,* xiv. 865.

[16] *Ibid.* xvii. 2962.

[17] *Monatsh. Chem.* vi. 490.

[18] *Ann. d. Chem.* cclx. 318.

[19] *Compt. rend.* cviii. 946.

[20] *Ibid.* lxxxix. 419.

[21] *Ibid.* xci. 118.

[22] *Chem. Soc. Trans.* 1887, p. 576.

[23] *Proc. Amer. Acad. of Sciences,* 1894, p. 369.

[24] *Archiv. Sci. Phys. Nat.* [2] xxvi. 89.

[25] Mean of results obtained by Wills, Brauner, Hauer, Staudenmaier, Gooch and Howland-Chikashigé, ranging from 125·4 to 127·3 (H = 1).

ATOMIC WEIGHTS RECALCULATED—*continued*

—	H=1	O=16	—
Terbium	158·8	160	Boisbaudran[1]
Thallium	202·61	204·15	Crookes,[2] Lepierre[3]
Thorium	230·87	232·63	—
Thulium	169·40	170·70	Cleve[4]
Tin	118·15	119·05	Bongartz and Classen[5]
Titanium	47·79	48·15	Thorpe[6]
Tungsten	183·43	184·83	Pennington, Smith and Desi[7]
Uranium	237·77	239·59	Zimmermann[8]
Vanadium	150·99	51·38	Roscoe[9]
Ytterbium	71·88	173·19	Nilson[10]
Yttrium	88·35	89·02	Cleve,[11] Jones[12]
Zinc	64·91	65·41	Richards[13]
Zirconium	89·72	90·40	Bailey[14]

[1] *Compt. rend.* cii. 396; cxi. 474.

[2] *Phil. Trans.* 1873, p. 277.

[3] *Bull. Soc. Chim.* [3] ix. 166.

[4] *Compt. rend.* xci. 329.

[5] *Berichte*, xxi. 2900.

[6] *Chem. Soc. Trans.* 1885, p. 108.

[7] *Amer. Phil. Soc.* 1894.

[8] *Ann. d. Chem.* ccxxxii. 299.

[9] *Chem. Soc.* 1868, pp. 330, 344.

[10] *Compt. rend.* xci. 56.

[11] *Bull. Soc. Chim.* xxxix. 120.

[12] *Amer. Chem. Jour.* xvii. 154.

[13] *Proc. Amer. Acad.* 1893, p. 200; *Zeitsch. anorg. Chem.* x. 1.

[14] *Proc. Roy. Soc.* xlvi. 74.

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